Preparation of Thermoplastic Vulcanizates from Devulcanized Rubber and Polypropylene

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

One of the current problems faced by mankind is the problem of safe disposal of waste rubber. Statistics show that the number of waste tires is continuously increasing at a very rapid rate. Since rubber materials do not decompose easily (due to their crosslinked structure), they end up being a serious ‘environmental problem’.

An intuitive solution to prevent the accumulation of the scrap tires is to continuously reuse them. A new patented reclamation method was discovered in our laboratory, which makes use of a twin screw extruder (TSE) in order to produce reclaimed rubber (referred as devulcanized rubber (DR) from here on) of very high quality. Also, this method has proven to be more economical than other commercial reclaiming methods. Products made solely from a reclaimed material face challenges from those made by virgin materials because of relatively poor properties. However, the striking advantage of using reclaimed rubbers is the cost reduction. Hence, it is important to work on establishing methods by which these reclaimed rubbers could be efficiently used and incorporated into present day products. The deterioration of properties could be minimized by blending them with varying amounts of other materials. A possibility in this direction is manufacturing of thermoplastic vulcanizates (TPVs) using reclaimed rubber and general purpose thermoplastics.

In accordance with this idea, the focus of this research is to prepare DR and polypropylene (PP) based TPVs. DR is unique as the rubber itself consists of two phases- one phase consisting of uncrosslinked (including devulcanized rubber molecules), and the other phase consisting of crosslinked (un-devulcanized) rubber. These un-devulcanized crumbs act as stress concentrators because they do not break-up easily, and lead to poor physical properties. Hence, this project tries to find out ways to increase the interfacial adhesion between the rubber and PP by using reactive and non-reactive techniques.

Preliminary experiments were carried out in a batch mixer to compare DR and rubber crumb (CR). DR based TPVs showed better properties than CR based TPVs, however, the properties were not useful for commercial applications. Sulphur based dynamic vulcanization was studied in a batch mixer and found to be not effective in improving the properties of DR based blends. On the other hand, DCP/ sulphur based curing system was found to show significant improvement in properties. Therefore, DCP/sulphur based curing package was studied in detail on the blends consisting of DR and PP. The optimum ratio of DCP/sulphur was found to vary depending on the ratio of DR/PP. A hypothesis regarding the mechanism of DCP/sulphur curing has been proposed, which seem to correlate well with the experimental results observed. Additionally, it was determined that DR prepared from tire rubber (DRT) performed better than DR prepared from waste EPDM (DRE) for the curing system used. Accordingly, experiments on a TSE were carried out using DRT and a combination of compatibilizing resins and curatives. This combination showed a drastic improvement in blends properties and once again the optimum ratio of compatibilizing resins seemed to depend on the ratio of DRT/PP.

As a result of the work, successful strategies based on reactive compatibilization techniques were developed in order to prepare useful TPVs having up to 70% DR. A series of compatibilization techniques has been evaluated using design of experiments and various characterization techniques such as mechanical tests, scanning electron microscopy, thermal analysis and crosslink density measurements. This led to the development of a formulation, which could improve the blend properties significantly. A tensile strength of around 10 MPa and an elongation-at-break of 150-180 % could be achieved for devulcanized rubber (70%) based TPVs, which has broadened the scope for its commercial applications. In addition to that, the process was established on a TSE that has enabled a continuous and steady production of these TPVs with reasonable throughputs.

Acknowledgements

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Dedication

Dedicated to the field of Rubber Recycling ….

Table of Contents

List of Figures

List of Tables

List of Abbreviations and Symbols

ASTM	American society for testing and materials
ABS	Acrylonitrile Butadiene Styrene
AE	Acetone extractable
A-HDPE	Acrylic-modified high density polyethylene
BE	Breaking energy
BR	Butadiene rubber
°C	Degrees Celsius
C-C	Carbon Carbon bond
C-S-C	Carbon Sulphur Carbon bond
COPE	Copolyesters
COPA	Copolyamides
CR	Crumb rubber
DCP	Dicumyl peroxide
DF	Degree of freedom
DOE	Design of experiments
DMTA	Dynamic mechanical thermal analysis
DR	Devulcanized rubber
DRE	Devulcanized rubber from EPDM
DRT	Devulcanized rubber from tire rubber

DSC	Differential scanning calorimetry
DVB	Divinyl benzene
E’	Stiffness elastic modulus (Pa)
E’’	Loss modulus (Pa)
EB	Elongation at break (%)
EDX	Energy-dispersive X-ray spectroscopy
ENG	Engage® 8200
EPR	Ethylene propylene rubber
EPDM	Ethylene propylene diene rubber
EV	Efficient vulcanization
EVA	Ethylene vinyl acetate
GTR	Ground tire rubber
HDPE	High-density polyethylene
IIR	Isobutylene-isoprene rubber
LDPE	Low density polyethylene
LOF	Lack of fit
LLDPE	Linear low-density polyethylene
MAPP	Maleic anhydride grafted polypropylene
MFI	Melt flow index (g/min)
MFR	Melt flow rate (g/10 mins)
MP	Melting point

MS	Mean sum of squares
N	Screw speed
NR	Natural rubber
NBR	Acrylonitrile butadiene rubber
PBD	Polybond® 3200
Phr	Parts per hundred rubber
PP	Polypropylene
PS	Polystyrene
PE	Polyethylene
Q	Feed rate
RMA	Rubber Manufacturers Association
R-EPDM	Raw EPDM
RR	Recycled rubber
S	Sulfur
SBR	Styrene-butadiene rubber
SBC	Styrene butadiene copolymer
SBS	Styrene-butadiene-styrene
SD	Standard deviation
SEM	Scanning electron microscopy
SRP	Scrap rubber powder
SSE	Single screw extruders

St. A	Stearic acid
$scCO_2$	Supercritical carbon dioxide
$SnCl_2$	Stannous chloride
Sol	Soluble
SS	Sum of squares
T	Temperature
TAC	Triallyl- cyanurate
tan δ	Loss-factor
TBBS	N- tert-butyl-3-benzothiazole sulfonamide
TDF	Tire-derived fuel
TE	Toluene extractable
Tg	Glass transition temperature
TM	Tensile modulus (MPa)
TP	Thermoplastic
TPE	Thermoplastic Elastomer
TPO	Thermoplastic olefin
TPU	Polyurethane
TPV	Thermoplastic vulcanizates
TS	Tensile strength (MPa)

TSE	Twin screw extruder
US	United States
WTR	Whole tire reclaim
W-EPDM	Ground waste EPDM
XE	Xylene extractable
ZnO	Zinc-oxide

Chapter 1

INTRODUCTION

1.1 Motivation

One of the current problems faced by mankind is the problem of safe disposal of waste rubbers. A major contribution in this area comes from used tires. Statistics show that the number of waste tires is continuously increasing at a very rapid rate. This can be attributed to the boom in the automobile industry and the trend continues to look upwards. Since vulcanized rubber does not decompose easily (due to their crosslinked structure), piling up of waste rubber is a serious ‘environmental problem’.

Landfilling is one of the early ways of disposal of discarded rubber products, which has continued to be among the top three major ways of disposing waste tires. But with the decreasing scope of available sites and corresponding cost explosion, this process of waste rubber disposal is no longer feasible. In addition to this, tires discarded in landfills tend to float on top and serve as breeding grounds for mosquitoes and rodents. Various compounding ingredients in the tires such as stabilizers, flame retardants, colorants, plasticizers etc. may leach out from the bulk to the surface. These small molecular weight additives are not eco-friendly and may kill advantageous bacteria of soil. In this way, landfilling causes serious environmental problems. Additionally, such sites are prone to cause catastrophic fire hazards. In fact, some countries have already banned the use of discarded tires for land filling.

An intuitive solution to prevent the accumulation of the scrap tires would seem to continuously reuse them. This would be possible if the scrap tire rubber is modified such that products made from it have acceptable properties. A process, which partly accomplishes this modification, is called reclamation, and the material so obtained is called reclaimed rubber. Although such a material resembles a virgin rubber, it remains quite inferior to the virgin rubber. A new (patented) reclamation method was discovered in our lab, which makes use of a twin screw extruder (TSE) in order to produce reclaimed rubber (referred as devulcanized rubber (DR) from here on) of very high quality. Also, this method has proven to be more economical than other known commercial reclaiming methods.

After the scrap rubber is modified to a reusable form, the next step is to commercialize it so that it can be continuously used up in the market. Products made solely from a reclaimed material face challenges from those made by virgin materials because of the decrease in the mechanical properties. However, the striking advantage of using reclaimed rubbers is the cost reduction. Hence, it is important to work on establishing methods by which these reclaimed rubbers could be efficiently used and incorporated into present day products. A possibility in this direction is manufacturing of thermoplastic vulcanizates (a blend of rubber and plastic) using DR and general purpose thermoplastics. Thermoplastics vulcanizates (TPVs) have a huge market, and preparation of TPVs from DR would open-up a broad range of applications for this material and would be a great step forward for the rubber and plastic industries. Needless to mention, the project would significantly help in reducing land pollution.

1.2 Research Objectives

In accordance with the above aim, this research focuses on finding strategies to prepare useful blends using technologically incompatible DR and polypropylene (PP), which is a cheap and easily available general purpose plastic. A proper control of overall blend morphology and good adhesion between the phases are required in order to achieve good mechanical properties. Various compatibilization techniques can be explored to improve the compatibilization between DR and PP. Processing variables such as processing temperature, feed rate, shearing rate etc. also play a crucial role in determining the properties of TPVs. Thus, there is a lot of scope to optimize all those factors in order to develop a stable extrusion process in which DR and PP could be blended. The main objectives of this work are as follows:

- To design a compatibilization system so that the two phases (DR and PP) blend with an acceptable degree of compatibilization indicated by useful properties
- To compare the performance of TPVs made from DR produced from tire rubber (DRT) and those made from waste EPDM rubber (DRE)
- To optimize the processing conditions in order to establish a continuous and stable extrusion process to produce DR based TPVs

A measure of the success would be the mechanical properties that would be achieved. As ASTM-D1566 defines an elastomer as a material having 100% elongation-at-break, achieving that in DRT based TPVs would mark a success for the project.

1.3 Thesis Outline

The thesis is divided into eight chapters. Chapter 1 introduces the importance and challenges of the project. Chapter 2 provides a glimpse of the research done so far across the world in the similar area, and explains some of the basic terminologies and relevant theory. Chapter 3 talks about the materials, equipments, characterization and processing methods used in this project. Chapter 4 describes the exploratory work done on dynamic vulcanization and various compatibilization techniques. In Chapter 5, the presented work dealt with implementation and optimization of a compatibilization technique, which was found most effective to blend DR and PP. Chapter 6 summarizes the comparison made between devulcanized rubber produced from tires (DRT) and devulcanized rubber prepared from waste EPDM rubber (DRE). The developed technique was translated onto a TSE, and further optimization of the material and processing variables was carried out, which is detailed in Chapter 7. Chapter 8 provides the concluding remarks considering the results obtained from all the experiments conducted. Towards the end, a few areas of the project where research can be directed in the future are touched upon.

CHAPTER 2

LITERATURE REVIEW

2.1 Scrap Rubber Statistics

To encourage recycling of waste tires and to abate tire dumps stockpiles, a bill [1] was introduced to the Unites States (US) Senate in which the congress identified the following:

1. US generates approximately 250,000,000 waste tires each year with over 3,000,000,000 waste tires stored or dumped in aboveground piles across US
2. Current waste tire collection and disposal practices present a substantial threat to human health and the environment
3. Waste tire piles are a breeding habitat for disease-carrying mosquitoes, rodents, and other pests and may be ignited causing potentially catastrophic fires
4. There are substantial opportunities for recycling and reuse of waste tires and tire-derived products, including tire retreading, asphalt pavement containing recycled rubber, rubber products, and fuel.

Rubber Manufacturers Association (RMA) estimates that about 4 megatons of tires were generated in the US in 2007 [2]. The scrap tire generation rate has steadily increased along with the population in the US. Based on the data reported to RMA through the state survey process, one tire is discarded annually per person in the US.

Figure 2.1 shows that the annual generation of tires in 2005 is around 299 million tires and the end use market consumed about 259 million tires. There is an eight–fold increase in percentage of consumption of scrap tires by the end use market annually since 1990.

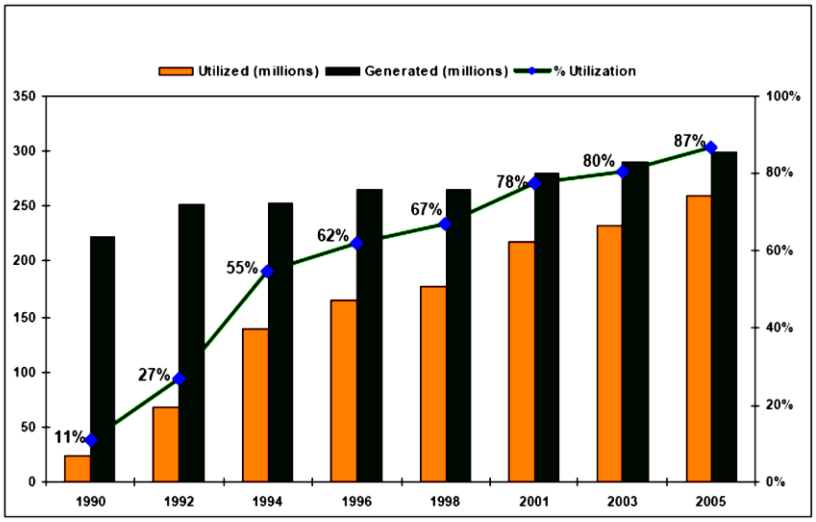


Figure 2.1 US Scrap tire management trend [2]

Figure 2.2 lists the various disposal ways of scrap rubber in 2007. It is noted that the biggest consumer of scrap tire was tire-derived fuel (TDF) followed by ground rubber and land disposal in the same order. While there were continued improvements in the efficiency of the scrap tire infrastructure, likely the most significant factor in the increased use of TDF was the price of energy. For the past many years, the marketplace witnessed unprecedented increases in prices for energy, most significantly the price of a barrel of oil, which drew upwards the prices of all other energy sources [2].

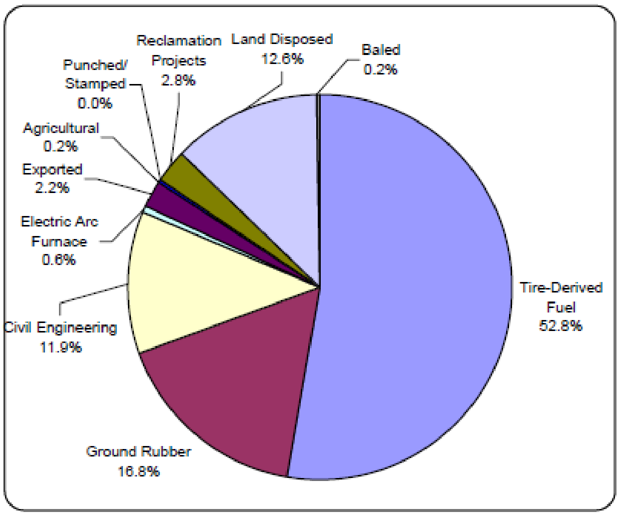


Figure 2.2 US Scrap tire disposal, 2007 [2]

In the ground rubber market there are two classes of particle sizes: ‘ground’ (10 mesh and smaller) and ‘coarse’ (4 mesh and larger, with a maximum size of one-half inch). Each of these size ranges has distinct market applications. Over the last few years, there has been significant growth in the market share of coarse sized particles. This particle range is used in playground surfacing, running track material, soil amendments etc. The smaller particle sizes are used for the more traditional applications such as asphalt rubber and molded and extruded rubber products [2].

By the middle 1980s, less than 1% of the worldwide polymer consumption was in the form of reclaim. At the beginning of the 20th century half of the rubber consumed was in the form of reclaim. It is expected that in the 21st century most of the scrap rubber will be recycled in the form of reclaim because of day to day increase in environmental awareness [3].

2.2 Reclamation

2.2.1 Vulcanization

Charles Goodyear (1800–1860) invented the vulcanization of rubber, when he heated a mixture of rubber and sulfur [4, 5]. Vulcanization is a process in which crosslinks are formed between polymer chains. These crosslinks can be of various types, but the most common type is the sulphur crosslinks, which require presence of unsaturation (Figure 2.3). Since most general purpose rubbers have unsaturation in the chain, sulphur is widely used for curing purposes. It was discovered that sulphur combined in the vulcanization network may be present as mono-sulphide, disulphide, poly-sulphide, cyclic sulphides and pendent sulphides. As seen in Figure 2.3, the value of sulphur atoms (x) in a crosslink for an efficient accelerated curing system is about 1 or 2, with little or no cyclic groups formed. In inefficient systems, x equals up to 8 and many cyclic structures are formed.

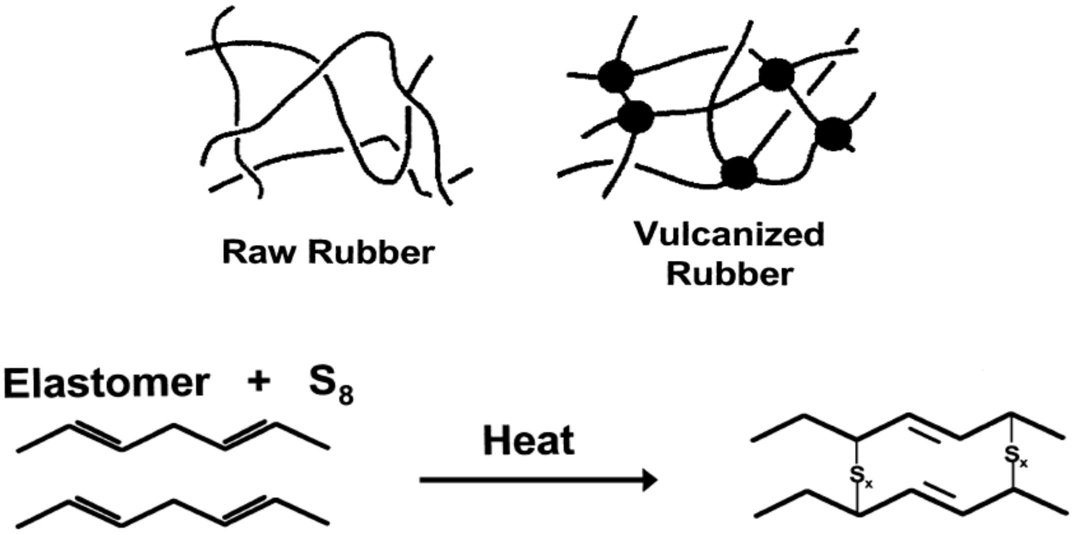


Figure 2.3 Crosslinks formed between polymer chains due to vulcanization [4]

Hence, depending on the ratio of sulphur to accelerators, the curing system can be categorized as efficient (EV), semi-efficient (semi EV) and conventional (Table 2.1). Accelerators are chemicals, which in combination with curing agents, increase the rate of vulcanization and in many cases the physical properties are also improved. On the other hand, accelerator activators are chemicals, which form chemical complexes with accelerators and thus aid in obtaining the maximum benefits from an acceleration system by increasing the vulcanization rate. The theory behind the sulphur vulcanization is very complex and not touched upon here. It is the three dimensional network which makes the vulcanized rubber a thermo-set and also provides its strength and many more required properties [4].

Table 2.1 Sulfur vulcanization systems and the resulting crosslinked structure [4]

Type	**Sulfur (S) (Phr)**	**Accelerator (A) (Phr)**	**A / S ratio**	**Poly and Disulfidic crosslinks**	**Mono-sulfidic crosslinks**
Conventional	2.0-3.5	1.2-0.4	0.1-0.6	90%	5%
Semi-EV	1.0-1.7	2.5-1.2	0.7-2.5	50%	50%
EV	0.4-0.8	5.0-2.0	2.5-12	20%	80%

*Phr denotes parts per hundred rubber

2.2.2 Types and Properties of Reclaimed Rubber

There are many types of reclaimed rubber depending on the source of the material. Broadly, they can be classified as the following:

- Whole Tire Reclaim (WTR): This is produced from tires and contains approximately 40% rubber hydrocarbon and the remaining 60% includes valuable carbon black, a little mineral filler, and softeners.
- Tire Tread Reclaim: This is produced predominantly from the tire-tread and do not require removal of textile. It may be specified as car or truck tread reclaims.
- Butyl Reclaim: These are produced from tire tubes, which are made of butyl rubber and hence butyl reclaim forms a category in itself.

Although reclaimed rubber is a product of discarded rubber articles, it has gained much importance as an additive in various rubber article formulations. Mechanical properties like tensile strength (TS), modulus, elongation at break (EB), resilience, tear resistance etc. are all reduced with the increasing amounts of reclaimed rubber in fresh rubber formulation. But at the same time, reclaimed rubber provides many advantages when incorporated into fresh rubber like the following [4, 5]:

- Reduced mixing time

Reclaimed rubber has a considerable stress history, i.e., it already goes through a large amount of mechanical work during manufacturing. Also, it contains all of the fillers, which were incorporated in the original compound. Hence, mixing time and power consumption are reduced considerably by its use in the compound. In addition to this, less heat is developed during mixing and subsequent processing, compared with compounds based on new rubber.

- Advantages during processing

Reclaimed rubber stocks can usually be processed at a lower temperature than those containing virgin rubber alone. This property is advantageously used in compounds having high carbon black content as such compounds tend to have scorch problems due to build up of high temperatures. Additionally, the gum strength of the rubber compound is improved significantly. Thus, they hold up their shape during processing and open steam cure, which is essential in extrusion products such as tubings. These compounds also show reduced die-swell and calendar shrinkage. That apart, reclaimed rubber promotes adhesion to textiles and hence, is preferred in compounds used in combination with textiles such as tires, conveyor belts etc. The use of a substantial proportion of reclaimed rubber in automobile floor mat stocks permits maximum calendar speed, which is sometimes twice as large as when very high proportions of virgin styrene-butadiene rubber (SBR) are used. Reclaimed rubber in tire carcass compounds gives better penetration in the fabric and chord than a non-reclaim compound.

- Influence on tack behavior

The tack of a non-reclaim compound may disappear within 24 hours after calendaring, while reclaimed rubber compounds tend to maintain their tack longer than non-reclaim compounds. Non-reclaim compounds become tackier in hot weather and dry in cold weather, whereas, reclaimed rubber compounds are less influenced in tack variation in hot and cold weather. This characteristic of reclaimed rubber is exploited for its usefulness in pressure sensitive adhesive tapes.

- Influence on curing and aging

Compounds containing reclaimed rubber help to retard and reduce sulfur bloom from both uncured and cured stocks. They cure faster than virgin rubber compounds, probably due to their combined sulfur and active crosslinking sites. Their usefulness in commercial purpose hence comes directly from the energy savings thus obtained. During vulcanization, reclaimed rubber containing stock show less tendency to revert, indicating better aging resistance.

Ball and Randall [6], De et al. [7, 8] and Dierkes [9] observed higher anti-aging characteristics of reclaimed rubber. As per Ball and Randall [6], such aging resistance of reclaimed rubber is due to the severe treatment of oxidation, heating, digestion and mechanical shearing, which appear to stabilize the hydrocarbon against further changes. Adhikari et al. [10] observed around 90% retention of tensile properties of reclaimed natural rubber (NR) and styrene butadiene rubber (SBR) without using any antioxidant.

2.2.3 Reclamation Methods

Reclaimed rubber is prepared by treating the ground vulcanized rubber by either solely or with a combination of thermal energy, mechanical energy and chemical agents in order to break the three dimensional network. A substantial regeneration of the rubber compound to its original plastic state is effected, yielding a product known as ‘reclaim’ or ‘reclaimed’ rubber. This material can then be reprocessed, compounded and re-vulcanized.

There are many methods of reclaiming rubbers and all basically lead to some kind of chain scission reactions in the compound. Reclaiming processes may be broadly classified into two groups: Thermo-chemical reclaiming processes and thermo-mechanical reclaiming processes [4]. In a thermo-chemical process, chemicals are added along with thermal energy to break the crosslinked network. In a thermo-mechanical process, stresses are used along with thermal energy to reclaim the waste rubber (i.e. to break down the three dimensional network). Due to the breaking of the network structure, the rubber macromolecules are transformed into smaller molecular weight fragments. Some of the common reclamation methods are described here:

Thermo-Chemical Reclamation Methods [1]

- Digester process/ Acid process/ Alkali process/ Neutral process

This process consists of two stages. In stage one, textile is removed using acid, alkali or zinc chloride. In the second stage, the ground rubber is loaded into a digester along with water, reclaiming oils, and other additives, such as activated carbon black. The digester is a cylindrical jacketed pressure vessel fitted with a horizontal agitator, and steam can be supplied to both interior and jacket, thus enabling a uniform temperature. The content is then heated to about 190 °C and maintained at this temperature for 3 or more hours with continuous agitation. The digester is then blown down and the contents deposited onto a conveyor. Necessary adjustments to the specific gravity and plasticity are carried out by addition of plasticizer, carbon black, or fillers, and the stock is then automatically conveyed to extruders for straining and refining.

- Pan Process

The ground rubber (fabric free) is intimately mixed with reclaiming chemicals and loaded onto steam vulcanizers. They are then subjected to steam heating at pressures in the order of 15 Bars at 180°C for 4-12 hours. This is followed by straining and refining in the conventional manner.

- Engelke Process

This process is the only one, which does not require the raw material to be fabric free. The scrap is subjected to very high temperatures (above 250 °C) for short periods of time (approximately 10-20 minutes) in small autoclaves. Fibers are carbonized in situ throughout the mass. The cracked stock is then premixed with plasticizing oils and peptizers and the reclaim is then strained and refined in the usual manner.

Thermo- Mechanical Reclamation Methods

- Mixing mill

In this process, crumb rubber is placed in an open two-roll mixing mill and milling is carried out at high temperatures (around 200 °C). A drastic molecular weight breakdown takes place due to mechanical shearing at high temperatures. In one patent by Maxwell [11], a physical process of reclaiming vulcanized rubber and refining of the reclaimed rubber is described. In the process, ground tire rubber was fed in particulate form together with reclaiming agents to a passageway between a smooth stator and a cylindrical rotor arranged to provide an axial shear zone and frictional heat. De and co-workers [7, 8 and 10] reported a mechanical reclaiming process of vulcanized NR. The reclaimed NR was prepared by milling vulcanized sheets at about 80 °C. The Mooney viscosity (> 200) of the reclaimed rubber was found to be very high indicating that the plasticity of rubber was very low due to the presence of higher percentage of crosslinked rubber.

- Microwave Technique

The microwave technique [12–14] has an advantage of being able to give a controlled dose of energy at specified frequency. Thus, a control over the amount of energy can be useful to make sure that only specific crosslinking bonds are broken. In this process, elastomer waste can be reclaimed to a material capable of being recompounded and revulcanized having physical properties essentially equivalent to the original vulcanizate. This method provides an ecologically sound method of reusing elastomeric waste to return it to the same process and products from which it was originally generated. It produced a product with equivalent physical properties as of the starting material. The reclaimed rubber is not degraded, which normally occurs in the other usual commercial processes. It is claimed that sulfur vulcanized elastomer containing polar groups is suitable for microwave devulcanization. Tyler and Cerny [14] claimed their microwave process as a method of pollution controlled reclaiming of sulfur vulcanized elastomer containing polar groups. The microwave energy devulcanization device generates heat at a temperature in excess of 260°C to yield a mass, which is fed to an extruder that extrudes the rubber at a temperature of 90–125 °C. The extrudate can be used per se as a compounding stock.

- Ultrasonic Energy

The first work with ultrasonic energy was reported by Pelofsky [15] in 1973, which was patented. In this process, scrap rubber was subjected to a source of ultrasonic energy, whereby, the bulk rubber effectively disintegrated upon contact and dissolved into the liquid. Ultrasonic irradiation used was about 20 KHz and with a power intensity of greater than 100 W. A similar ultrasonic reclaiming process of NR vulcanizate was reported by Okuda and Hatano [16] and Isayev [17], which were also patented. Later on Isayev and co-workers have carried out several studies using ultrasonically reclaimed rubber [18-20].

- Twin-Screw Extrusion

The most recent development in the field of reclaiming is exploring devulcanization of scrap rubber using a twin-screw extruder (TSE). Devulcanization can be described as a reclamation process, which predominantly breaks the crosslinking sulphur bonds rather than the main backbone chains (Figure 2.4). Such a material is termed as devulcanized rubber (DR). Many studies were recently done in this area considering that the scission is predominantly occurring in the crosslinks and the polymer molecules remain intact, therefore providing a better strength. The idea of this process lies in cleaving of the crosslinks rather than the polymer chains as shown below.

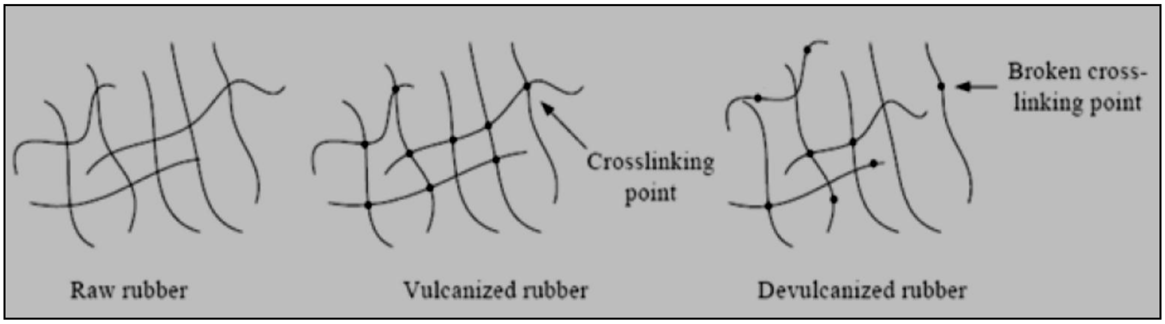


Figure 2.4 Effect of reclamation on crosslinks in polymer chains [21]

A probable way of preparing a DR is by breaking the carbon-sulphur (C-S) bond or sulphur-sulphur (S-S) bonds. It is known that C-C, C-S, and S-S bonds have different bond strengths. Although the differences are not significant, an effort can be made to break selectively only the C-S and S-S bonds. Mouri et al. [21] found a purely mechanical method to devulcanize EPDM using a modular screw type of reactor. The temporal changes in the rubber matrix during dynamic devulcanization under a typical test condition were studied by pulling out the screw quickly from the barrel of the reactor on the way, and sampling the materials along the axial length of the screw (Figure 2.5). Changes in the gel content and crosslink density during the process from section B to D were calculated (Figure 2.6). The gel fraction and crosslink density decreased until position C, finally reaching 45%. Thus, it was concluded that the gel fraction decreased as devulcanization progressed and its crosslink structure gradually became weaker.

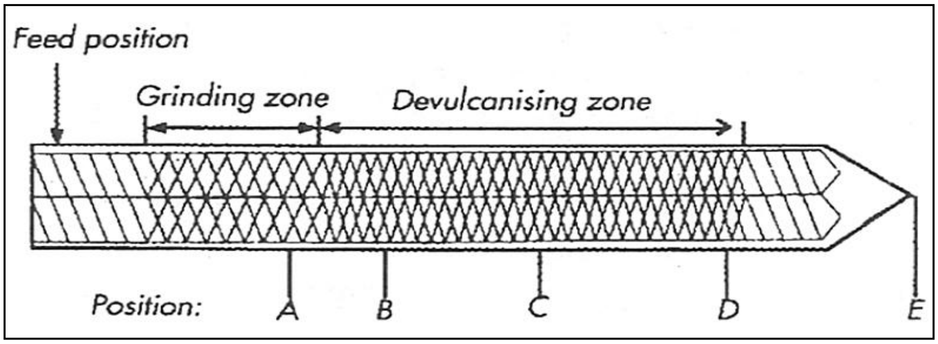


Figure 2.5 The zones across the screw of the extruder as demarcated by Mouri et al. [21]

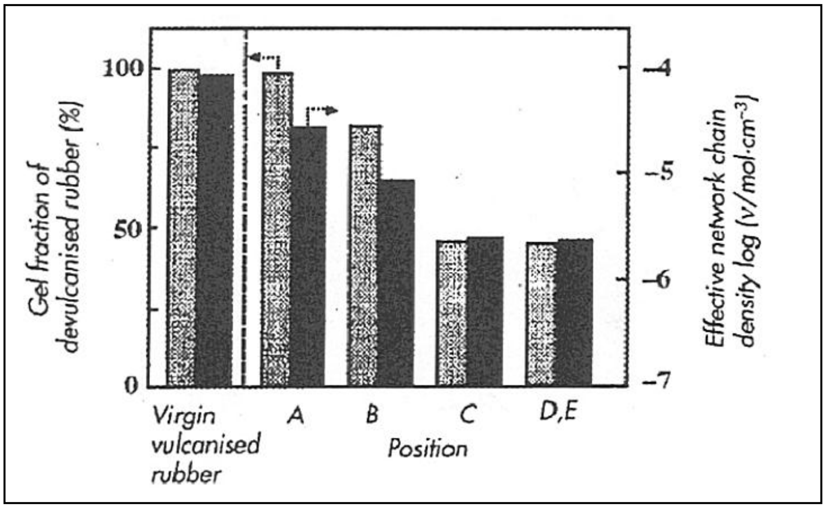


Figure 2.6 Effect of devulcanization on gel fractions and crosslink density [21]

Apart from this, a study was also made on the total number of poly, di and mono sulfidic bonds. It was found that, initially there was a rise in monosulfidic bonds and simultaneous decrease in polysulfidic bonds. Later on, as the devulcanization proceeded, the mono-sulfidic bonds also diminished to almost zero. It was claimed that the sulphur was stabilized by combining with hydrogen (Figure 2.7).

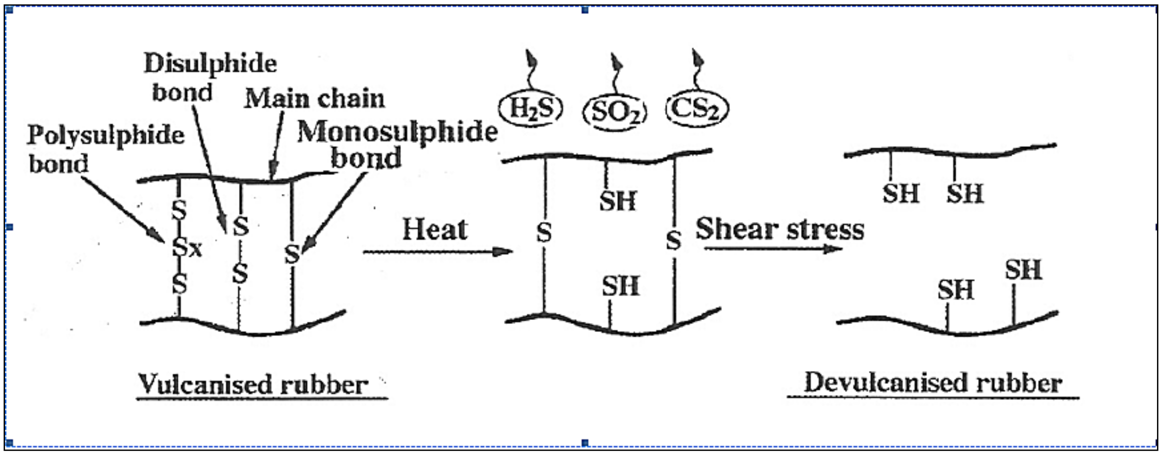


Figure 2.7 Stabilization of sulphur by reacting with hydrogen [21]

Fukumori and Matsushita [22] further developed the same technology, which was presented by Mouri et al [21]. They utilized a TSE and optimized the devulcanization process by adjusting different parameters like shear stress, temperature and internal pressure. They tried three different screw configurations, three different temperatures and two different screw speeds and concluded that with optimized screw geometry and configuration, selective breakage of crosslinking points in the waste can occur predominantly under suitable conditions of temperature, shear stress and internal pressure. According to them, at extremely high shear stress most of the rubber molecules became fully elongated to their limited extensibility and the bond having the lower elastic spring constant became the most extended as compared to other bonds having higher elastic constant. As the elastic constants for C-C bond is 100 and S-S bond is 3 (Figure 2.8), hence, the elastic energy induced by high shearing may be particularly concentrated at the S-S bonds selectively, causing their scission.

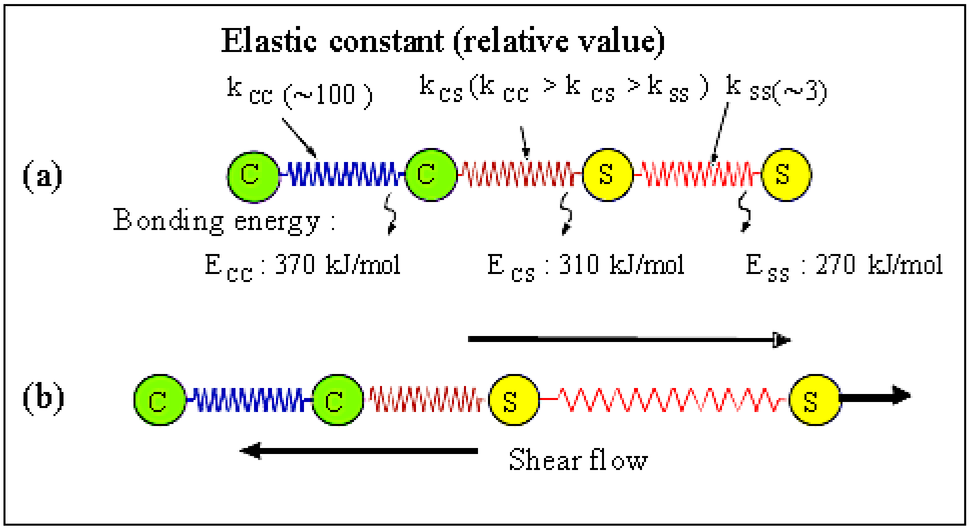


Figure 2.8 Breaking of crosslink points in high shear flow: (a) model for the network chain (b) deformation of network chain (particularly, C-S bonds) by shearing [22]

In another study, Fukumori et al. [23] carried out continuous devulcanization experiments on three kinds of waste rubbers (based on NR, SBR and iso-butyl isoprene rubber (IIR)). They could efficiently control various kinds of chemical reactions by optimizing the parameters in the reactor such as shear stress, temperature and internal pressure. Continuous devulcanization was carried out using a modular screw type of reactor. It was found that for NR and SBR based DR, the retention of both the TS and EB was more than 90% at a content of up to 30 phr. For the IIR based rubber, DR exhibited tensile properties comparable to those of new IIR.

Kojima et al. [24] developed a devulcanization process that utilizes supercritical carbon dioxide ($scCO_2$) along with a devulcanizing reagent (thiol amine, diphenyl disulphide etc) in a pressurized autoclave. In this case, $scCO_2$ was used in order to improve the impregnation or diffusion of the devulcanizing agents. The sol fraction was found to be less than 52% and dramatically increased at around the critical pressure for $scCO_2$. Hence, it was concluded that the devulcanizing reagents such as diphenyl disulphide penetrated into the inner part of the vulcanized rubber together with $scCO_2$, which resulted in enhanced rate of the devulcanization reaction. They also found that it is easier to devulcanize compounds consisting of polysulphidic bonds rather than those having mono-sulphidic bonds.

A number of studies have been carried out using $scCO_2$ to facilitate polymer processing [25-30]. Tzoganakis discovered that use of $scCO_2$ during extrusion promotes devulcanization by swelling the polymer [31]. A significant reduction in viscosity led to believe that $scCO_2$ behaves as a solvent and penetrates the polymer chains causing them to swell. This was believed to have two effects- the swelling would put the less elastic C-S and S-S crosslinks under more stress and the swollen polymer would be more susceptible for cleavage of these crosslinks. Based on this technology, Tzoganakis and Zhang [32] carried out studies on devulcanization of rubber on a TSE with help of $scCO_2$. The work by Tzoganakis was further developed by Meysami [33, 34], and the process was scaled up onto an industrial scale TSE, from which a reasonably high throughput of DR was obtained. It was shown that throughput can be increased to an optimum level and the ratio of Q and N (Q being the feedrate while N being the RPM of the screw) along with the process temperature are important parameters. The DR obtained could be re-vulcanized again by adding curing agents, and it showed reasonable rheological, physical and mechanical properties.

2.3 Thermoplastic Vulcanizates

Thermoplastic elastomers (TPEs) are materials that behave as plastics at high temperature and rubbery at room temperature. They combine the improved impact resistance of an elastomer and strength of a thermoplastic. Such materials offer a short product cycle time in manufacturing due to rapid melt hardening on cooling. There are various types of TPEs such as block copolymers (styrenic based (SBC), polyurethane based (TPU), copolyesters (COPE), copolyamides (COPA)) and polymer blends based [35]. Polymer blends based TPEs can be subdivided into thermoplastic olefins (TPOs) and thermoplastic vulcanizates (TPVs). TPOs are generally made by melt-mixing rubber with thermoplastics. They have both the elastomeric and semi-crystalline polyolefin phase as continuous and both these phases flow during processing. On the other hand, TPVs have the elastomeric phase crosslinked and discontinuous in a continuous plastic phase. In such blends, only the plastic phase is believed to flow during processing. Some of the significant improvements of TPVs over TPOs are reduced permanent set, improved ultimate mechanical properties, improved fatigue resistance, greater resistance to attack by fluids, (for example hot oils), improved high temperature utility, greater stability of phase morphology in the melt, greater melt strength and more reliable thermoplastic fabricability. Since the introduction of proprietary products such as Santoprene® (by ExxonMobil) prepared by the dynamic vulcanization of blends containing PP and EPDM, much commercial interest had developed in dynamic vulcanization.

2.3.1 Preparation, Processing and Compounding of TPOs/ TPVs

There are many ways of preparing TPEs. These methods are broadly divided into chemical and mechanical methods [35]. Chemical methods include arranging the elastomer and plastic monomer units during polymer synthesis itself. On the other hand, mechanical methods include simple melt mixing at the melting temperature of the thermoplastics in a batch mixer or extruder. Mechanical methods are commonly used to prepare TPOs and TPVs. There are a few ways of getting cured rubber domains in TPVs. One of the ways of preparing TPVs, which was used in this project, is by dynamic crosslinking of the rubber phase by addition of curatives during melt mixing. Another way is to mix partially vulcanized rubber with the molten plastic. TPOs/ TPVs are always dried before processing in order to remove moisture. The processing character of TPOs/ TPVs is mainly determined by the processing behavior of the thermoplastic phase. For example, EPDM/ PP TPV has the same processing temperature as that of PP. Molding and extrusion is also carried out in the same manner as for PP and hence, the processing cost is lower than that of thermosets. Some processing factors that affect TPV morphology and properties are:

- Screw design: Screw element configuration controls the pressure inside the barrel and also the shear stresses applied to the material. A higher shear stress results in smaller rubber particles, which would result in more uniform distribution of rubber domains in the plastic phase. Such a material shows better qualities in terms of mechanical properties.

- Feed rate: Feed rate controls the fill factor inside the extruder, which in turn influences the stress experienced by the material.
- Screw speed: Screw speed is one of the prominent factors, which decides the magnitude of shear rate being applied to the material, again affecting the size of rubber domains in the plastic phase.
- Temperature: Temperature imparts a thermal stress on the various chemical bonds and hence, too high temperatures may lead to thermal decomposition of the bonds. Hence, when working with DR, operating temperature was always kept less than 300 °C.

To obtain the desired properties, reinforcing fillers may be added to the TPOs/ TPVs. Desired properties may include changes in TS, hardness, modulus, tension set, EB etc. Fillers are added before curatives and after sufficient melt mixing of the components is carried out, curatives are added within a short time.

2.3.2 Morphology of TPOs/ TPVs

In order to prepare blends with useful properties, rubber and plastic used in the preparation should be very compatible. It is difficult to determine the extent of compatibility required between rubber and plastic phases for preparing TPOs/ TPVs with good physical properties and processability. A variety of additives can be used to promote compatibility by reducing the interfacial tension. These additives can be broadly divided into two groups- ‘non-reactive compatibilizers’ and ‘reactive compatibilizers’. A nonreactive compatibilizer, as the name suggests, does not chemically react with the components. They reduce the interfacial tension by spreading at the interface and mixing with both phases through their component parts, which are similar to one phase or the other. This category includes external plasticizers or polymeric materials such as a copolymer (preferably a block copolymer, which has chain units similar to both components of the blend). Tri-block copolymers (such as styrene-ethylene-butylene-styrene) and graft copolymers are also used. The “in situ” formation of a block or graft copolymer by blending suitable functionalized polymers is known as reactive compatibilization. This is realized through covalent or ionic bonding during the melt blending of suitably functionalized polymers. For instance, maleic anhydride grafted polypropylene (MAPP) is often used as a compatibilizing agent for EPDM and PP.

It is very important that the two phases, i.e., the elastomeric and plastic phases are inter-dispersed uniformly as this provides a better quality material [36]. During melt mixing, the dispersion of the phases is better, if the viscosities of the phases are similar. That apart, the ratio of the polymers being mixed also has a significant importance upon the end morphology of the TPOs/ TPVs. Morphology is also affected by the cross link density, type of crosslinks and presence of additives such as fillers, plasticizers, compatibilizers etc. It was confirmed by Coran and Patel that addition of compatibilizers help in obtaining good phase morphology [37]. Numerous studies [38-51] were carried out using curing systems based on phenolic resins, sulphur, peroxide and so on, which shall be elaborated on the following chapters.

TPVs have been prepared from a great number of plastics and elastomers, however only a limited number of them have technological importance. A study of 99 elastomer-plastic combinations (9 kinds of elastomer and 11 kinds of plastic) was done based on mechanical properties of the TPV and related to characteristics of their elastomeric and plastic components [52]. The conclusion of the work was that the best combinations were those in which the surface energies of the plastic and elastomer were matched, the entanglement molecular length of the elastomer was low and the plastic was at least 15 % crystalline.

In case of TPVs, use of proper type of crosslinks is essential in strengthening the elastomer phase to a maximum. It is preferable to have selective crosslinking of the rubber phase and therefore care has to be taken while choosing the curing system. Fully curing the rubber phase and controlling the size of rubber particles to 1-2 microns or less improves the material properties. It is preferred to have very small particle size of the elastomeric domains as the smaller the size is, the higher the strength. The size of the rubber particles and the degree of cure has significant influence on material properties. There is a considerable increase in interfacial area between rubber and plastic phases due to break up of the rubber phase into small particles. Smaller rubber particles also facilitate deformation by relatively thin PP ligaments. Generally, the larger the rubber particles, the poorer are the mechanical properties of TPOs/ TPVs.

During cooling of plastic/ rubber blends, voids may be created due to differential shrinkage between plastic and rubber. Although there is considerable shrinkage in the plastic phase from melting point to crystallization temperature, once the morphology is frozen, the rubber particles shrink more than the plastic on cooling to room temperature and hence, moving away from the plastic phase. This phenomenon caused due to differential thermal shrinkages, facilitates rubber debonding from the matrix under the application of stress [53].

For TPVs to show good elastic properties, the interphase between the two phases should provide a high degree of adhesion. It is preferred that the plastic phase has a high crystallinity and a reasonable melting temperature. A high crystallinity ensures that the material has enough strength and crosslinks (in form of crystalline domains). On the other hand, crystallinity also determines the melting temperature of plastic phase, which sets the upper service temperature for the material.

2.3.3 Studies on Reclaimed/ Ground/ Devulcanized rubber based TPO/ TPVs

Jacob et al. [54] studied processing, cure characteristics, and mechanical properties of EPDM (ethylene propylene diene) rubber containing ground EPDM vulcanizate of known composition. Mixing was carried out on a two roll mill and all compositions were subjected to various tests. They found that the Mooney viscosity increased and scorch time decreased by the addition of the ground vulcanizate. Also, at higher loadings (above 50 phr) of the ground rubber, the maximum torque decreased due to the filler effect. Upon addition of ground waste rubber, stress-strain properties and tear resistance increased, whereas, heat build-up marginally increased, resilience marginally decreased and abrasion resistance decreased. The same group also observed the effect of incorporating ground EPDM vulcanizate in place of virgin rubber in an EPDM/ PP TPV composition [55]. The TPV composition of EPDM/ PP= 70/30 was chosen and the mixing was done in a Brabender Plasticorder and DCP system was used for dynamic vulcanization. The ratio of the rubber content in the waste EPDM (W-EPDM) to the raw EPDM (R-EPDM) in the blends was varied from 0: 100 to 45: 55. The blends of R-EPDM/ W-EPDM at a constant rubber/ plastic ratio of 70/30 showed typical TPV morphology with finely divided rubber phase dispersed in a continuous plastic phase. Their attempts to replace higher amounts (more than 45%) of R-EPDM by W-EPDM failed as the processing became extremely difficult. Interestingly, a drop in mechanical properties occurred at lower loadings of W-EPDM, but the properties showed an improvement at intermediate W-EPDM loadings.

Kim et al. [56] studied the influence of screw configuration on the morphology and mechanical properties of waste EPDM/polyethylene and polypropylene copolymer blends in the ratio range of 70/30 and 75/25 in order to develop high-value blends from waste EPDM. In order to improve the mechanical properties of the material, extrusion was carried out with different screw configurations. It was deduced that as the number of kneading disks increased, dynamic vulcanization of the rubber phase increases as the shear stress and residence time of the blend increases. This improved the mechanical properties of the TPOs/ TPVs produced.

Kumar et al. [57] worked on manufacturing of low density polyethylene (LDPE) based TPOs/ TPVs, containing virgin rubber and ground tire rubber (GTR) with and without dynamic curing. The composition of the blends remained constant - LDPE: fresh rubber: GTR= 50: 25: 25. SBR, NR and EPDM were used as fresh rubber sequentially. Dynamic curing was done using either sulphur or peroxide systems. GTR was mechanically degraded using mixing mill and then GTR/ elastomer master-batches were melt blended with LDPE in a Brabender Plasticorder. It was concluded that the efficiency of degradation and devulcanization of GTR was of crucial importance in production of good TPOs/ TPVs. Based on the thermo-mechanical and mechanical properties of the resulting TPOs/ TPVs, they found that the best performance was achieved by recipes containing GTR and EPDM after dynamic vulcanization with sulphur. This was attributed to the presence of EPDM, which acted as a suitable compatibilizer between the plastic phase and GTR.

Mennig et al. [58] prepared TPOs/ TPVs from blends of PP and powdered rubber waste. The idea behind their work was that if one assumes that the characteristic feature of a TPV is the presence of crosslinked elastomer particles dispersed in PP, it is then possible to make materials of this type by blending ground recycled rubber with molten PP. An internal mixer was used for carrying out the mixing under specific conditions. After this, the blend was cooled, granulated and processed by a ram-screw injection moulding machine. Various combinations of curing agents such as sulphur, sulphur/ peroxide, sulphur/phenolic resins were used. It was found that in all cases there is chemical grafting of the PP on the surface of the particles of the comminuted rubber. The degree of grafting was greater than 65% in the composition containing cumyl peroxide and about 40% in cases where sulphur or sulphur plus cumyl peroxide are used. When phenol formaldehyde was used, the grafting of PP was negligible. It was proposed that grafting in the blends not-containing cumyl peroxide may be caused by the activating effect of the peroxide groups probably present on the surface of the comminuted material. These authors concluded that although the TS of these materials was not very high, optimizing the ratio of comminuted rubber to polyolefin and amount of crosslinking system can improve the blend properties.

Ismail and Suryadiansyah [59] prepared TPOs/ TPVs based on PP/ NR and PP/recycled rubber (RR) blends. Fine rubber powder was obtained from the sanding process of polishing rubber balls. This was used to prepare PP/ RR blends using different reclaim rubber content and similar blends using NR were also prepared. The results indicated that at similar rubber content, PP/ RR blends have higher TS and Young's modulus, but lower EB and stabilization torque than PP/ NR blends. It was suggested that in PP/ NR blends, the molecular entanglements in the rubber chains alone are unable to prevent rapid flow and fracture in response to applied stress, causing lower tensile stress and Young's modulus. On the other hand, in PP/ RR blends, the presence of crosslinked rubber powder and other curatives in RR was thought to be the reason for reaching higher TS.

Tanaka [60] developed a technology using a TSE, which consisted of devulcanization of EPDM waste, blending of the devulcanized EPDM and PP, and dynamic vulcanization of rubber phase leading to a TPV. The extruder was divided into various sections such as a pulverizing zone, a devulcanizing zone, a blending zone and a dynamic vulcanizing zone. Devulcanization was carried out using only mechanical energy considering that the elastic constants of S-S bonds and C-S bonds are weakest. In the dynamic vulcanizing zone, the rubber component was dynamically vulcanized by metering in the curatives and hence, TPV was formed having EPDM as the dispersed phase. It was found that important factors were screw configuration, screw rotation speed, barrel temperature, feedrate of material and compounding ingredients. Also, it was discovered that the degree of devulcanization of EPDM influenced the phase formation of the TPOs/ TPV. By mixing at high shear in the dynamic vulcanizing zone, surface appeared to be smoother as the revulcanized EPDM phase was finely dispersed. The material obtained exhibited good material properties comparable to those of commercial TPVs.

Luo and Isayev [61] carried out several experiments to prepare TPVs from ultrasonically DR (produced from tread and sidewalls of passenger and truck tires) and PP. In addition to that, DR was compounded and revulcanized after blending with PP. A few compatibilizers were used along with curatives, which were based on sulphur and phenolic resin. The study concluded that phenolic resin cure system gave the better results along with maleic-anhydride modified PP used as compatibilizer. TS increased with an increase in dosage of modified PP, however, EB was not found to show any consistent trend (Figure 2.9). Additionally, batch mixed samples gave a same or better EB than those mixed in TSE, whereas, TS values for the samples produced in the two processes were similar. The properties of the samples prepared from injection molding were found superior to the ones prepared from compression molding, probably due the orientation effect induced during injection molding.

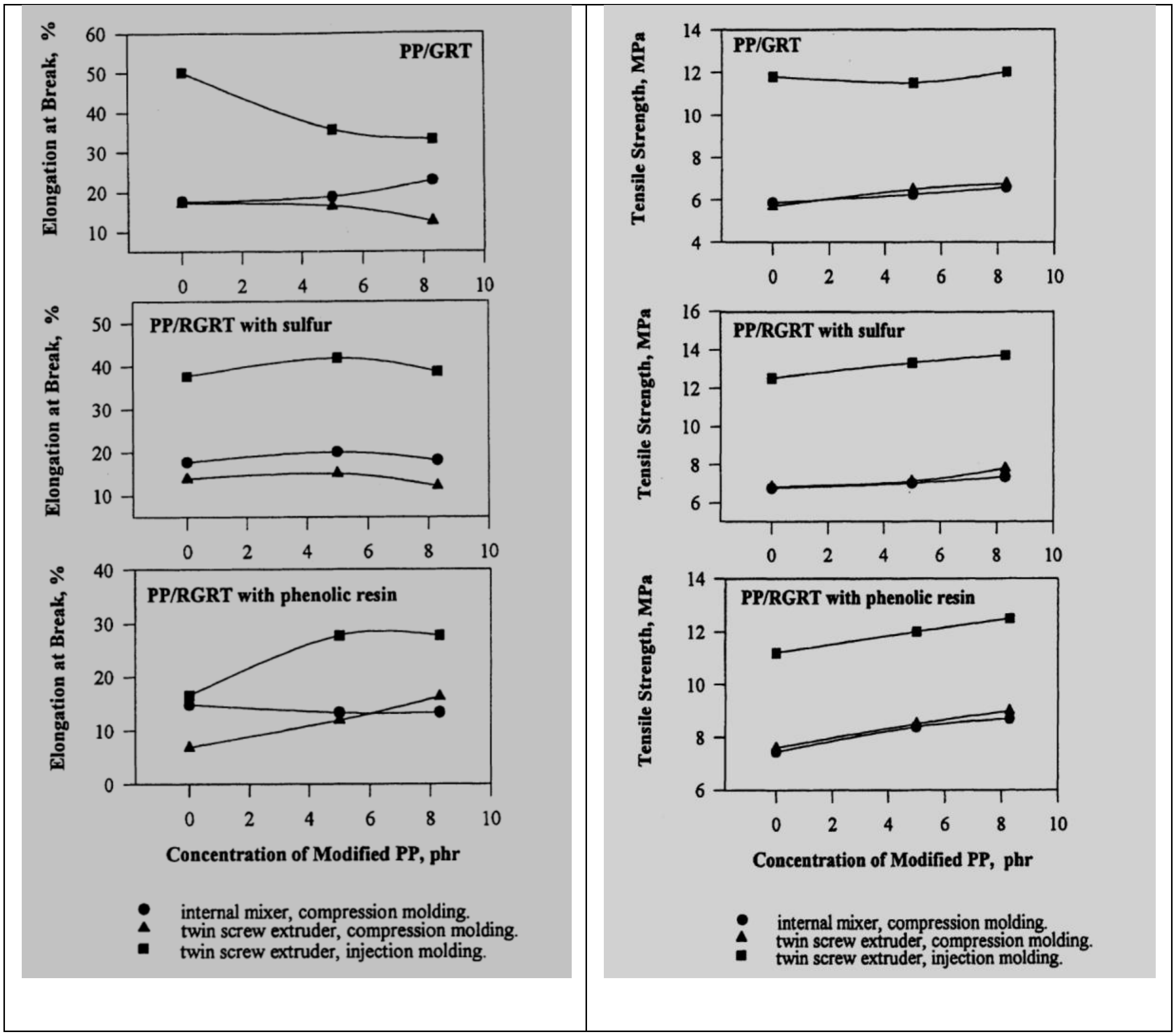


Figure 2.9 Effect of modified PP dosage on EB and TS [61]

Li et al. [62] studied the effect of ethylene–propylene–diene terpolymer (EPDM), dicumyl peroxide (DCP), and dimethyl silicone oil on the mechanical properties of high-density polyethylene (HDPE) composites filled with 60 mesh cryogenically scrap rubber powder (SRP). The addition of 10 wt % EPDM, 0.2 wt % DCP, and 4 wt % dimethyl silicone oil significantly increased both the impact strength and EB of HDPE/ SRP composites. Both, EB and TS, showed significant drop with increase in dosage of SRP. It was noted that unmodified rubber gave higher TS than modified (having the additives stated earlier) one, but vice-versa was true for EB (Figure 2.10).

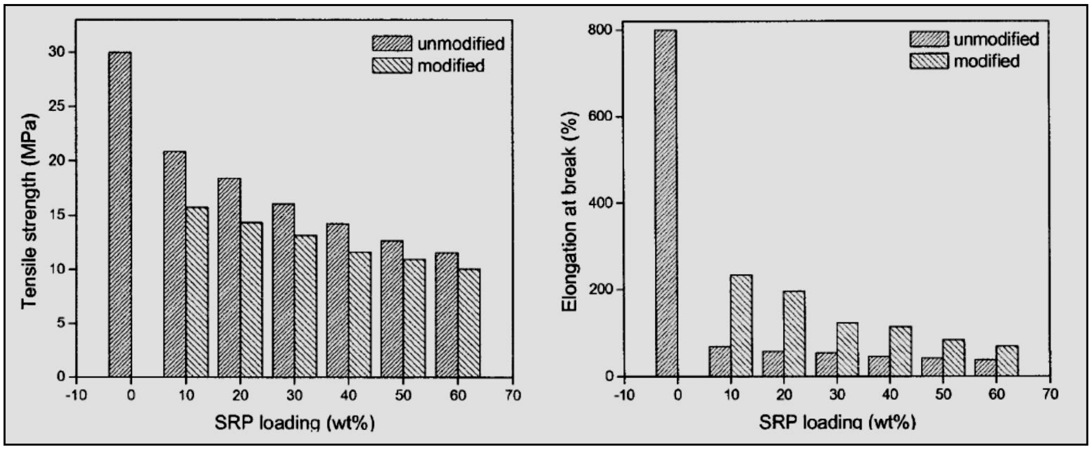


Figure 2.10 Effect of dosages of recycled rubber on TS and EB of HDPE-SRP composites [62]

Qin et al. [63] prepared blends using linear low-density polyethylene (LLDPE) and GTR with the dosage of GTR being 60%. The effects of kneading time and functional polymers (as compatibilizers) on the mechanical properties of the blends were investigated. It was found that the blend, which contained styrene-butadiene-styrene (SBS) copolymer as compatibilizer, with a kneading time of 20 minutes, behaved best with regard to mechanical properties. It is preferable to have selective crosslinking of the rubber phase and therefore care has to be taken while choosing the curing system. They found that the kneading time had a greater effect on EB values than TS (Figure 2.11).

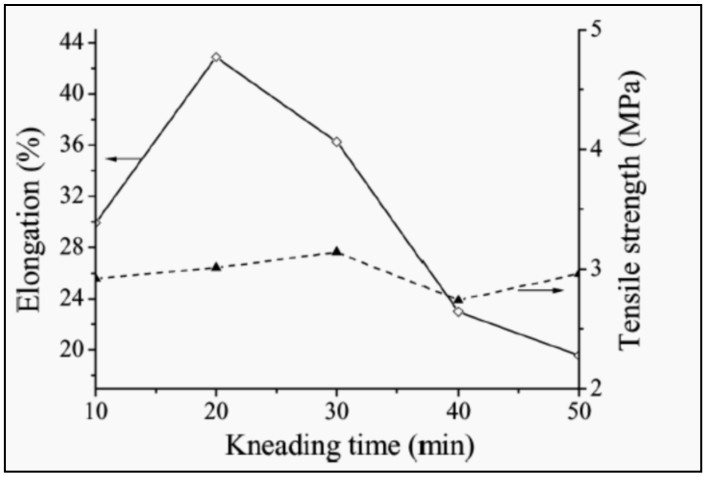


Figure 2.11 Effect of kneading time on TS and EB [63]

Zhu and Tzoganakis [64] prepared TPVs from PP and reclaimed GTR crumbs. Three types of interfacial strengthening agents - degraded PP, hydrosilylated PP, and hydrosilylated PP grafted onto SBR—were prepared in the melt via a stepwise series of reactions, and employed to generate various degrees of interfacial adhesion in the aforementioned blends. The incorporation of the interfacial agents resulted in improvements in the mechanical properties of these TPVs, even though the rubber particle size remained constant. It was concluded that the PP chain length and the functional groups present in the interfacial agents affected the magnitude of the improvement in the mechanical properties.

Naskar et al. [65] prepared rubber-plastic blends, wherein the rubber phase consists of a mixture of EPDM and GTR. The plastic phase consisted of acrylic-modified high density polyethylene (A-HDPE). The blends with higher rubber content showed poor processability and physical properties, while the compositions with higher plastic content behaved like toughened plastics. However, the rubber/ plastic= 60:40 blend was found to behave as a

TPOs/ TPV, and it was observed that 50% of EPDM can be replaced by GTR having equivalent rubber hydrocarbon content without deterioration in properties

Seok and Isayev [66] prepared PP/ GTR blends using a TSE. The blends were then passed through a reactor to devulcanize GTR, after which, the blends were dynamically revulcanized using an internal mixer. Under optimal conditions of ultrasonic treatment, the mechanical properties of the blends were improved in comparison with their earlier experiments.

Liu et al. [67] carried out experimental investigation to evaluate the use of recycled rubbers in blends for the development of new TPOs/ TPVs and rubber-toughened plastics. Recycled rubbers were obtained from various commercial sources and included representatives from the EPDM, SBR, and NR/ SBR blend families, as well as a range of particle sizes. A series of five different virgin polypropylenes (PP) were used as the plastic phase, representing a range of molecular weights and suppliers. Blends were prepared in a Haake batch mixer over a broad range of compositions. Compatibilization and reactive blending techniques (peroxide based for EPDM/PP and phenolic resin based of SBR/PP) were used to improve the quality of the scrap rubber/ plastic blends with respect to both mechanical and rheological properties. Results indicated that these blending techniques were required to obtain acceptable mechanical strength in the resultant materials. Additional parameters that significantly enhanced properties included elevating the blending temperature, reducing rubber particle size, and increasing PP molecular weight. This latter conclusion was attributed to a lower degree of crystallinity in the PP phase that contributes to a better blending between the phases. The positive effect of (t-butyl hydroperoxide based) reactive blending on mechanical properties is shown in Figure 2.12.

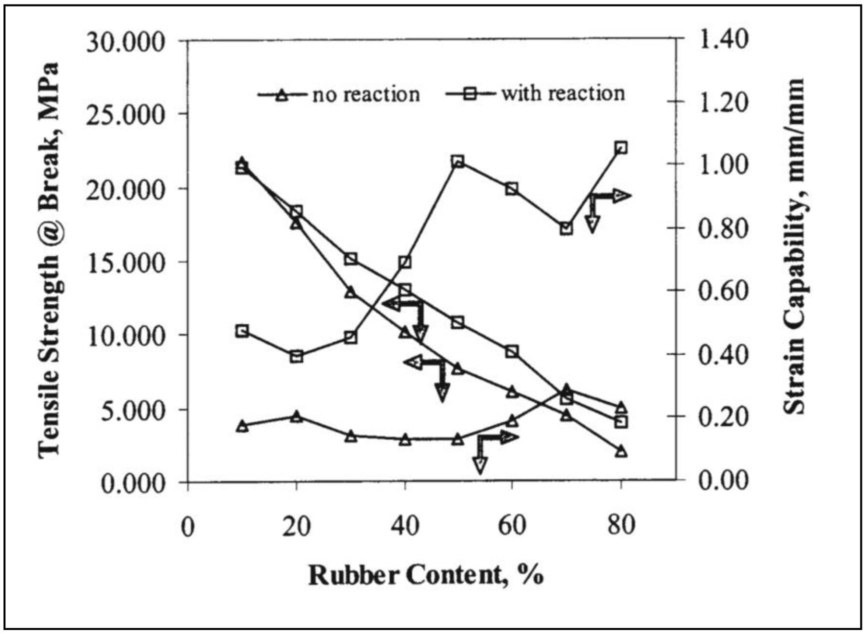


Figure 2.12 Tensile properties of EPDM/ PP blends illustrating effect of reactive blending [67]

2.3.4 Applications of TPOs/ TPVs

Since their introduction in 1981, TPVs have had a wide spectrum of use. They have been used as a direct replacement of thermoset rubbers. For many products, which do not require high temperature resistance, TPOs are sufficient. But for those products whose service conditions require high thermal resistance, TPVs are preferred. TPVs, characterized by complete crosslinking of the rubber phase in a continuous thermoplastic phase, perform well with regard to hot-oil resistance, compression set (at elevated temperatures), and high-temperature utility. Thus, TPVs more closely approach the performance characteristics of thermoset rubber than any other type of TPEs. TPVs have a niche over thermosets in terms of product fabricability, improved properties, price/ performance balance, and fabrication economics. They can be readily fabricated by blow molding, whereas, thermoset rubber cannot.

TPV products are used in underhood automotive appliances where temperatures reaches as high as 135°C to 150°C right from motor vehicle components to building construction, household appliances, electric cable, food packaging and hospital operating rooms. As time progressed, TPVs have moved beyond rubber replacement, especially where features such as colorability and soft touch of products are involved, such as, in automotive and consumer products [53].

2.4 Conclusion

There is a great potential for recycling waste rubber effectively from tire waste by reclaiming and blending them with thermoplastics. The rubber constituents in TPOs/ TPVs based on rubber-plastic blends can be replaced by the recycled rubber. However, blends need to be compatibilized to provide the desired level of performance. Thus, there should be continuous efforts to improve the blending technology in order to obtain blends with improved properties.

CHAPTER 3

EXPERIMENTAL

3.1 Procedures

3.1.1 Processing

<u>**Devulcanization of Crumb Rubber**</u>

As mentioned earlier, a process was developed in our lab for devulcanizing rubber crumb in a twin screw extruder (TSE), facilitated by $scCO_2$. Crumb rubber (CR) was fed into a 34mm diameter (Leistritz) TSE and $scCO_2$ was injected inside the barrel through a nozzle using a gas injection system (Figure 3.1). Devulcanized rubber (DR) was produced in form of strands or strips and cooled in a water bath placed downstream. This DR was blended with PP to prepare TPOs and TPVs in this project.

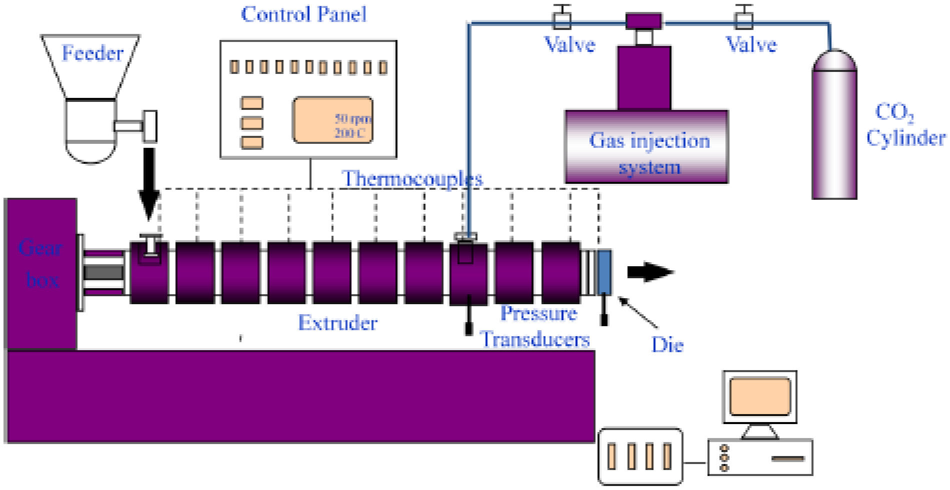


Figure 3.1 Schematic of the devulcanization process [1]

Batch Mixing of blends

Mixing was carried out in a Haake Rheomix-3000 (Figure 3.2) attached to Rheocord-90 (Haake) at 180 °C with the rotor RPM set to 80.

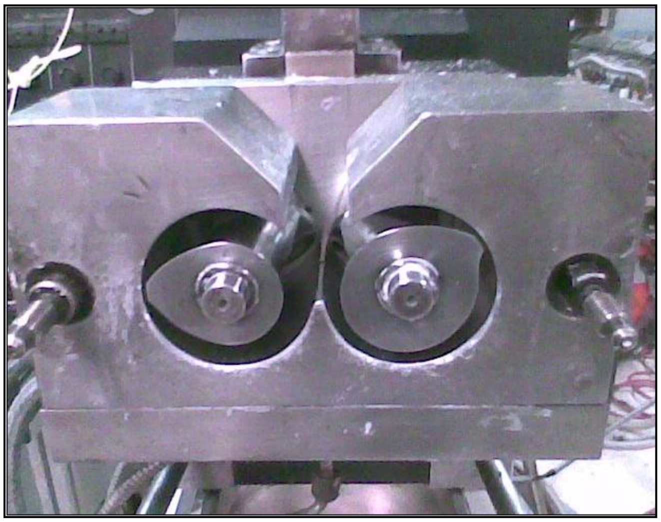


Figure 3.2 Batch mixer used for mixing with the rotors exposed

PP was added first into the batch mixer, and when the mixing torque became stable, measured amount of DR was added. After torque stabilization, curatives were added, whenever used. Subsequently, lumps of the material were taken out of the mixer and molded (at 180 °C) into a sheet at a pressure of 40,000 Psi. The mould was then allowed to cool to room temperature under pressure.

Continuous Mixing of blends

TSE was used in order to carry out continuous preparation of blends (Figure 3.3 and Figure 3.4). A physical mixture of PP and DR granules was fed into the main hopper upstream. This was allowed to plasticize and mix well along the length of the screw before addition of the curing package from a second open feeding point. The temperature of the zone, where the curatives were added, was set to room temperature in order to reduce the instantaneous flashing off of the curatives. The TPO/ TPV material was extruded in the form of strands through a die, and was cooled in a water bath to be pelletized later on.

Figure 3.3 Lab extruder set up showing the two feeding points

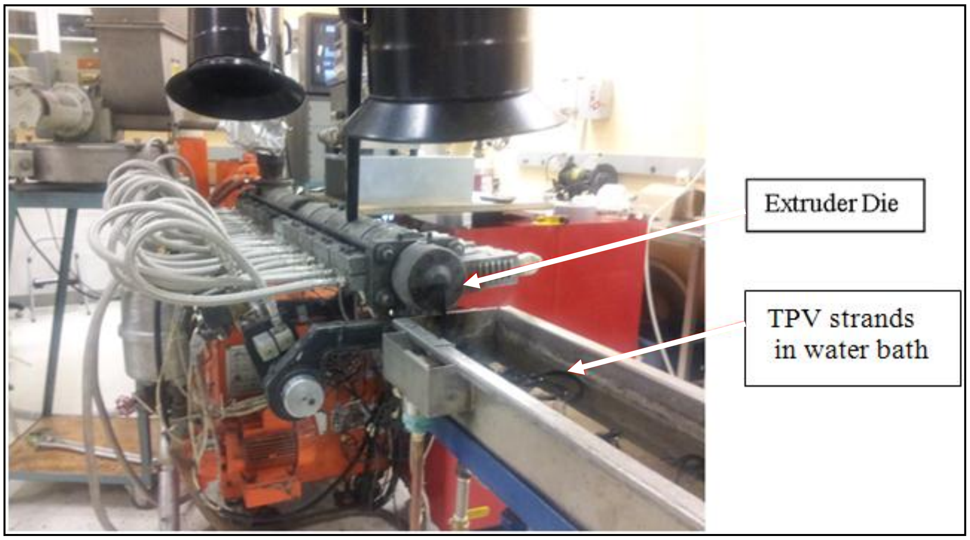


Figure 3.4 TPV strands in cooling water bath at the downstream end

3.1.2 Mechanical Properties

Tensile strength (TS) is the force needed to break the material. Elastomers with high ultimate tensile properties are stronger in stretching than an elastomer with lower values. Elongation at break (EB) gives a measure of how far a material can be stretched before it breaks. Usually, an increase in compatibility is accompanied with an increase in EB values. The area under the stress-strain curve gives the idea of toughness of the material (breaking energy (BE)). This gives an indication of the energy absorption capability of a material.

In order to measure those properties, a sheet was molded in a hydraulic press manufactured by Pasadena Hydraulics (Figure 3.5) at 180°C (unless mentioned otherwise), under a pressure of around 40000 Psi. Around 3-4 bumping or degassing operations were done to allow entrapped air to escape. After 10 minutes, heating was switched off, and the sample was air cooled with the pressure being maintained, as thermoplastics have a tendency to shrink upon cooling. Once cooled, the sheet was taken out of the mould and allowed to mature for a day, before cutting dumbbell specimens for tensile testing.

Figure 3.5 Hydraulic press used for molding sheets

Tensile testing was carried out as per ASTM D-412 [2] using an Instron 3365 unit. Dumb-bell shape specimens were cut from the molded sheets and subjected to tensile strain till the specimen broke. The dumbbell specimen is gripped between the jaws of the instrument and stretched at 500 mm/min until the sample ruptures. The instrument reports the TS, EB, and BE values. A typical plot (Figure 3.6) obtained from this instrument gives a graph between stress and strain. Three to four specimens for each sample were tested and the results were recorded as the average of the four values. An idea of the variability of results was obtained from the standard deviation (SD).

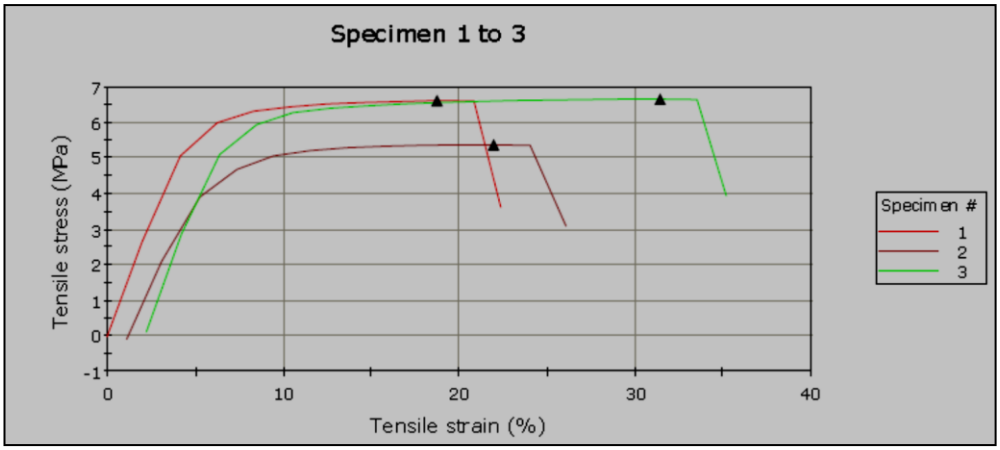


Figure 3.6 A typical plot as obtained from the tensile test

Compression set indicates the amount of permanent deformation that occurs when a material is compressed to a specific deformation, for a specified time, at a specific temperature. A high set value shows that the sample cannot recover to its original state after being subjected to compressive tension and this is usually not desirable (especially for sealing applications). ASTM D 395 [3] describes the standard test method for compression set measurement. The original thickness of the specimen was measured and then using the compression set device, which is shown in Figure 3.7, the specimen was compressed to 25% of the original thickness. The entire set-up with the specimen was placed in an oven at elevated temperatures (70°C) for a test period of 22 hrs. After that, the specimen was removed and cooled down to room temperature. Final thickness of the specimen was measured, and percent of permanent deformation was calculated based on the change in sample thickness before and after the test.

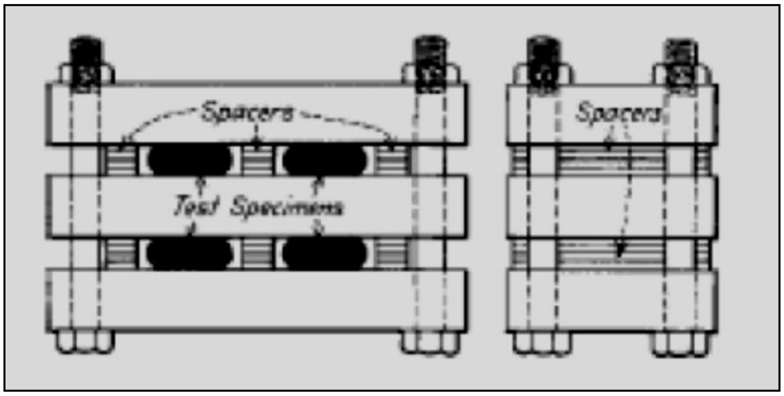


Figure 3.7 Compression set apparatus set up

The hardness of a material is one of the important criteria considered when choosing a TPE. Rubber hardness is often measured using an instrument called Shore durometer, which ha sa metal indenter that penetrates the surface of the material. Shore durometers come in a variety of hardness ranges. Shore A scale is used for softer materials and is scaled from 0 to 100; 0 is for extremely soft material and 100 is for a very hard rubber material. Shore A instruments are not as accurate when readings are above 90. For harder materials, the Shore D durometer is used, as it has a sharper indenter and a stronger spring to penetrate to a greater depth. A 5 mm thick material was placed under the Shore A durometer's (manufactured by Instrument & MFG Co/ Durotronic 2000) indenter and the readings were noted down. ASTM D 2240 [4] describes the standard test method for hardness measurement of rubber materials.

3.1.3 Thermal Properties

Differential Scanning Calorimetry (DSC)

The melting and crystallization behavior was studied using a TAI Instruments DSC Q2000. Around 5 to 10 mg of a material was taken and DSC scans were registered from -100 °C up to 200 °C at 20 °C/ min heating rate. The melting temperature was taken as the temperature corresponding to the maximum in fusion endotherm. Heat of fusion (ΔH) was calculated from the area under the endothermic peak. Degree of crystallinity was calculated as follows:

$$Crystallinity\ (\%) = \frac{\Delta H}{(\Delta H^{\circ})(wf)} \times 100\ ,$$

where, ΔH° is the heat of fusion of 100% crystalline PP taken as 207 J/ g [4] and wf is the weight fraction of PP in the blend. This method assumes that major contribution towards crystallinity comes from polypropylene.

Dynamic Mechanical Thermal Analysis (DMTA)

DMTA was used to study the viscoelastic behavior of the TPOs/ TPVs. Rectangular bars (10 mm x 5 mm x 2 mm) were subjected to oscillating tensile strain of 0.01% at a constant force of 25Kgs. Measurements were made at 1 Hz frequency and 1 °C/min heating rate over the temperature range -100°C to 30°C. Variation of the complex E-modulus and its constituents (viz. storage and loss moduli; E' and E", respectively) as a function of the temperature (T) were recorded. The mechanical loss factor, tanδ = E"/E', is an indication of the T_g of the material. ASTM D4065 [6] describes the method in detail.

3.1.4 Rheological Properties

Rheological properties determine the processing behavior of a material. TPVs exhibit a pseudoplastic behavior, i.e., the melt viscosity reduces with shear rate. Various factors such as size, shape, and distribution of the dispersed phase and interfacial adhesion between the components affect the flow behavior of polymer blends [7]. Rheology was studied using a capillary rheometer (Kayness Galaxy V 8502) at 200°C, with a die having a length of 1.2 inches and a diameter of 0.03 inches. Shear rate was varied from 0.55 sec^{-1} to 55.32 sec^{-1}. ASTM D3835 [8] describes the method to determine the properties of polymeric materials using capillary rheometer.

3.1.5 Morphology

Scanning electron microscopy (SEM) (by Zeiss Ultra Plus) was used to study the morphology of our samples. The acceleration voltage used for scanning with the electron beam was either 20 kV or 10 kV. Pictures at various magnifications were taken to understand the phase morphology. For carrying out SEM measurements, the samples were fractured after cooling in liquid nitrogen for 5 min. The fractured surfaces were stained with osmium-tetraoxide vapor for approximately one hour. Osmium-tetraoxide tends to react with double bonds and stain the region, which appears to be bright. Hence, one may assume that the brighter regions are the rubber phase where more osmium-tetraoxide has preferentially bonded. With the same logic, a dark region indicates no double bonds present in that area, likely where only PP exists or due to dilution of double bonds caused by an intimate mixing of the matrix and DR. In general, the lesser the difference in the contrast between the phases, the better is the degree of compatibilization. The DR phase contained rubber crumbs, which could not be devulcanized. As the compatibilization increases due to interfacial reactions, the double bonds reduce in concentration, and therefore, the crumbs look darker. One should be careful in interpreting the SEM results as the image obtained is only for one sample from the batch, which is assumed to be representative of the entire batch. Also, the darker regions of the SEM images have to be analyzed along with the shape and the size of the domain in order to speculate whether it is a darkened rubber crumb (unsymmetrical shape and a size beyond 5 microns) or PP phase.

3.1.6 Soluble Content

Extraction studies were carried out to analyze the weight loss and soluble (sol) content of the samples. Approximately, 4 grams (g) of a sample was taken in a cellulose thimble and soxhlet extraction using acetone was carried out for 16 hours. After this, the residue was dried in an oven at 60° C overnight. The dried sample was weighed, and a similar extraction was carried out using toluene. After that, the dried residue was packed in a thimble with glass-wool and submerged in boiling xylene for at least 8 hours. Acetone is believed to remove the low molecular weight components such as un-reacted chemicals, degraded polymer molecules, oils etc. Toluene is a good solvent to dissolve uncrosslinked rubber molecules, whereas, boiling xylene is a good solvent for uncrosslinked PP molecules. Hence, the residue after these three extractions is the gel portion which includes crosslinked rubber and PP. Figure 3.8 shows the Soxhlet extraction apparatus, which consists of an electric heater, 500 ml round boiling flasks, extraction tubes, and a condenser.

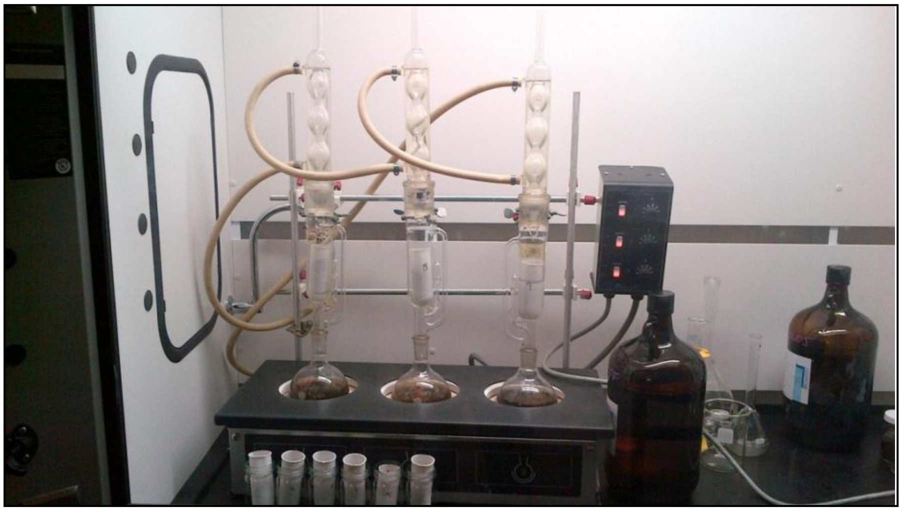


Figure 3.8 Soxhlet extraction apparatus

It should be noted that toluene extraction may not indicate the true value of uncrosslinked rubber content as the PP phase may shield the rubber chains from getting extracted by toluene and later on get extracted by xylene along with uncrosslinked PP. The sum of xylene and toluene extractables is known as soluble content (sol content), and the remaining unextractable content is the crosslinked portion (gel content).

3.2 Materials

3.2.1 Resins

The various resins used in this project along with their suppliers are tabulated in Table 3.1.

Table 3.1List of resins used

Resin	Supplier
Isotactic Polypropylene (PP31KK01, PH382M)	LyondellBasell
Maleic anhydride (2%) grafted polypropylene (Polybond® 3200)	Chemtura
Maleinized 1, 2 Polybutadiene (Ricobond® 1031), Flash point > 120°C	Sartomer
Polyethylene-octene copolymer (Engage® 8200 – melt index 5, 8480- melt index 1 at 190°C/2.16kg/10mins)	Dow Chemical
Devulcanized rubber from tire tread and EPDM	Tyromer Inc.
Styrene-butadiene rubber (1502)	International Specialty Products
Natural rubber (SMR 20)	RCMA Asia
Ethylene propylene diene rubber (K1200A)	DSM Elastomers
Ethylene vinyl acetate (Elvax® 260)	DuPont
Phenolic resin (SP-1045)	Plastics Engineering Company

3.2.2 Chemicals and Solvents

Table 3.2 indicates the chemicals and solvents used in this project along with their suppliers. The name of the supplier and purpose of application is also summarized.

Table 3.2 List of chemicals and solvents used

Name of the chemical	Supplier	Purpose of application
Zinc oxide (ZnO)	Fisher scientific	Rubber curing (activator)
Stannous chloride ($SnCl_2$)	Sigma Aldrich	Coagent
Stearic acid (St. A)	Fisher scientific	Rubber curing (activator)
TBBS	Airboss	Rubber curing (accelerator)
Sulphur (S)	Sigma Aldrich	Crosslinking agent
Osmium-tetraoxide	Sigma Aldrich	SEM Staining agent
Dicumyl Peroxide (99%)	Sigma Aldrich	Crosslinking agent
Trigonox® 311 (95%)	Akzonobel	Crosslinking agent
Trigonox® 145- E85 (85%)	Akzonobel	Crosslinking agent
Toluene (99%)	Sigma Aldrich	Solvent (sol content test)
Xylene (99%)	Sigma Aldrich	Solvent (sol content test)
Acetone (99%)	Sigma Aldrich	Solvent (sol content test)

CHAPTER 4

DYNAMIC VULCANIZATION AND COMPATIBILIZATION OF DEVULCANIZED TIRE RUBBER AND POLYPROPYLENE

4.1 Introduction

Chapter 2 (section 2.3) discussed the advantages of dynamic curing of TPOs. However, dynamic curing by itself may not improve the properties, if the polymer blends are very incompatible. Incompatible polymer blends often exhibit poor mechanical properties and their morphology is often characterized by phase separation and voids. Koning et al. [1], classified different polymer blends into three categories namely ‘completely miscible’, ‘partially miscible (compatible)’ and ‘immiscible’. Miscible blends display homogeneity at least at the nanometer scale, if not at the molecular level (example polystyrene and polypropylene oxide blend- Noryl). In the second group, part of one component is dissolved in the other, and the blend exhibits a fine phase morphology accompanied with satisfactory properties (example polycarbonate and acrylonitrile-butadiene-styrene terpolymer). Immiscible blends have coarse phase morphology (as the adhesion between phases is poor), so they cannot be used without a compatibilizer. Most polymer blends are immiscible and therefore need compatibilizers to achieve reasonable properties. Formation of two phase systems is not necessarily an unfavorable event since many useful properties, characteristic of a single phase, may be preserved in the blend, while other properties may be averaged according to the blend composition. Thus, controlled level of phase separation and good adhesion between the phases are required to achieve good mechanical properties. A strong interphase adhesion can assimilate stresses and strains without disruption of the established morphology [2]. Ajji and Utracki [3] pointed out that compatibilization reduces the interfacial tension, facilitates the dispersion, stabilizes morphology, and enhances adhesion between the phases, thus improving the properties of a blend.

Luo and Isayev [4] found that maleic anhydride grafted polypropylene (MAPP) significantly improved the mechanical properties of the PP/ GTR blends they worked with. Maleic anhydride groups reacted with the rubber phase, whereas, the PP component of MAPP interacted with PP phase, hence resulting in a better interphase. In their work, Kumar et al. [5] used virgin SBR, NR and EPDM for compatibilizing GTR/ LDPE (low density polyethylene) blends, and found EPDM to be the best compatibilizer. The efficiency of the virgin rubbers followed the ranking: EPDM > NR > SBR. The outstanding performance of EPDM was explained by its dual compatibility: molecular entanglement with the LDPE phase and interfacial sulfuric crosslinking with partly decomposed GTR. They found the sulphur cure to be better than the DCP cure system. Naskar et al. [6] also found virgin EPDM rubber as a good compatibilizer for GTR blends with high density polyethylene (HDPE). Virgin EPDM acted as a compatibilizer for waste EPDM and PP blends too as found by Jacob et al. [7].

In a research carried out by Grigoryeva et al. [8], GTR was reclaimed by preheating the GTR/ bitumen blend in 1: 1 ratio at 170°C for 4 hours in an oven. Bitumen was found to be able to reclaim GTR and improve the mixing of GTR with polyethylene (PE).

Mennig et al. [9] used various combinations of curing agents such as sulphur, sulphur/ peroxide, sulphur/ phenolic resins to prepare TPOs/ TPVs from blends of PP and powdered rubber waste. Li et al. [10] found a positive effect of using EPDM, DCP, and dimethyl silicone oil on the mechanical properties of HDPE composites filled with 60 mesh cryogenically scrap rubber powder (SRP). Zhu and Tzoganakis [11] prepared TPVs from PP and reclaimed GTR crumbs using three types of interfacial strengthening agents—degraded PP, hydrosilylated PP, and hydrosilylated PP grafted onto SBR. The incorporation of the interfacial agents resulted in improvement of mechanical properties.

Liu et al. [12] used compatibilization and reactive blending techniques (peroxide based for EPDM/ PP and phenolic resin based of SBR/ PP) to improve the quality of the scrap rubber/ plastic blends with respect to both mechanical and rheological properties. The group found the phenolic resin cure to be more effective than sulphur.

Thus, there are various methods to improve the properties of blends made from recycled rubber. This chapter presents the work done to investigate the influence of dynamic vulcanization and various compatibilization techniques on the properties of DRT based TPOs/ TPVs. As sulphur based curing system is most commonly used for dynamic vulcanization, a detailed investigation has been carried out to evaluate the performance of this system. That apart, a series of compatibilizers and curatives were selected to be tested based on the literature survey and knowledge of structure-property relationships.

4.2 Experimental

4.2.1 Materials

Resins and Chemicals

The PP used for the TPV preparation was PP31KK01 (Melt flow rate (MFR) = 5g/ 10 min). It had a TS of 25 MPa and an EB of 7.43%. The DRT used had a TS of 8.9 MPa and EB of 172% when cured with standard sulphur (S) based curing package (S= 1.5, TBBS= 1.5, ZnO= 3, St. A= 2 phr). Osmium-tetraoxide was used for SEM staining purposes.

Compatibilizers

The materials evaluated as compatibilizers were SBR, NR, EVA, EPDM, Engage® 8480 (polyethylene-octene copolymer), bitumen, Polybond® 3200 (2% maleic anhydride grafted polypropylene), Ricobond® 1031 (1, 2 polybutadiene), phenolic resin (SP-1045) and DCP.

4.2.2 Experimental design

The effectiveness of sulphur dynamic vulcanization was statistically evaluated. A mixture design was followed in order to evaluate the influence of dosages of sulphur, TBBS (N- tert-butyl-3-benzothiazole sulfonamide), PP and DRT on the mechanical properties of TPVs. Statistica software package was used to generate the mixture design points with four variables. The variables and their constraints provided to the software were: DRT 40% - 80%, PP 20%- 60%, S 0.5%-4%, TBBS 0.5%- 4%. The ranges for DRT and PP amounts were chosen based on the common compositions used for preparing TPO/ TPV blends. The constraints for S and TBBS were chosen based on typical dosages used in the industry. Dosages of ZnO and St. A were kept at a constant level, which were known to be sufficient (from preliminary experiments) for the ranges within which sulphur and TBBS were varied. Centre-point was replicated thrice to evaluate the lack of fit (LOF) of the model. Mixing was carried out on a Haake batch mixer at the conditions mentioned in Chapter 3.

That apart, experiments were carried out to evaluate the performance of reactive and non-reactive compatibilizers. For preliminary tests, single factor experiments were carried out in order to get an idea about the influence of a factor. The most effective compatibilizer system among the ones analyzed was tested at three ratios of DRT: PP (60: 40, 70: 30 and 80: 20). DR is pre-compounded with fillers and other additives, thus the actual hydrocarbon content is less than what is mentioned in the formulations. However, as the experiments mostly dealt with relative comparisons, this factor is not considered in the discussions.

4.3 Results and Discussion

4.3.1 DRT versus Crumb Rubber

It is essential to compare DRT with crumb rubber (CR) and virgin rubber (SBR in this case) to get an idea as to where it stands in terms of performance. As evident, DRT shows improvements in EB and TS, when compared to CR (Table 4.1), but is far inferior to virgin SBR. Addition of curatives did not improve the properties of DRT based blend, although it improved the properties of SBR based blend. This may be due to the presence of rubber crumbs in DRT, which continue to act as stress concentrators and hence, outweigh the effect of curative addition.

Table 4.1 TS and EB of DRT and CR based blends (Rubber: PP= 60: 40)

	A	B	D	E	F
SBR	100	...	100	....	...
DRT	...	100	....	100	...
CR	....	.....	...	...	100
PP	66	66	66	66	66
S	1.5	1.5	...	...	...
TBBS	1.5	1.5	...	...	...
ZnO	3	3	...	...	...
St. A	2	2	...	...	...
TS (MPa)	11.26 ± 1.5	6.77 ± 0.84	3.26 ± 0.16	6.48 ± 0.16	2.48 ± *
EB (%)	397 ± 70	7.8 ± 2.9	69.3 ± 16.6	19.5 ± 2.4	3.0 ± *

* Only one result could be obtained

4.3.2 Effect of composition

Figure 4.1 shows the effect of composition on TS and EB of cured DRT/ SBR/ PP blends. SBR consisted of 25% of the rubber phase in all blends. As expected, an increase in PP content increased TS and decreased EB. The curing package used was the same as given in Table 4.1. None of the compositions seemed to show useful properties.

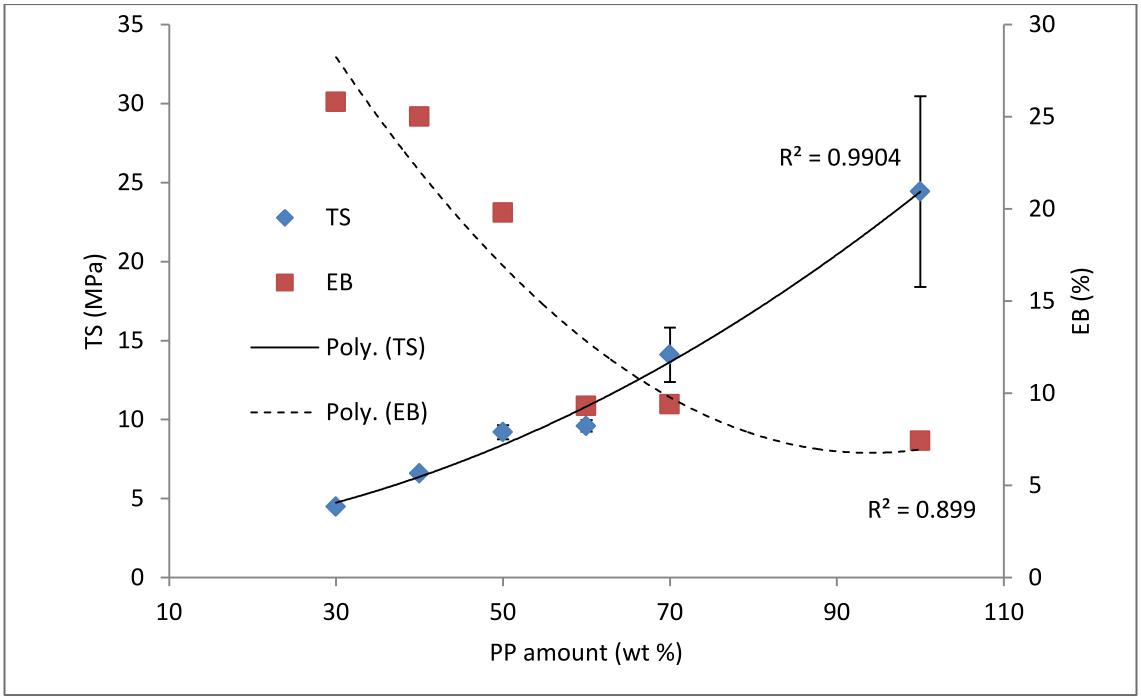


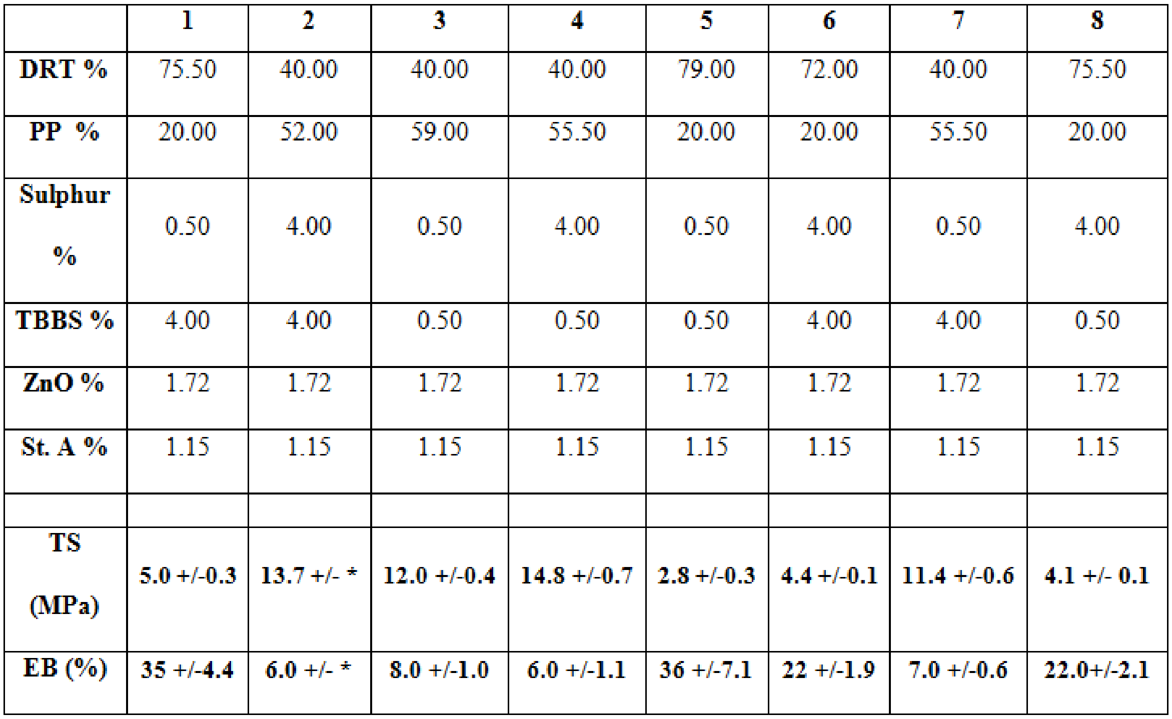
Figure 4.1 Effect of PP amount on TS and EB

4.3.3 Dynamic Vulcanization

Mechanical Properties

Mixture design results are shown in Table 4.2 and Table 4.3. The data were analyzed using Statistica software with TS and EB as the dependent variables. DRT, PP, S and TBBS were treated as the independent variables. Linear models indicated the LOF term as significant, therefore, quadratic models were fitted to TS and EB data. Table 4.4 and Table 4.5 show the overall fit of the quadratic models for TS and EB.

Table 4.2 Properties measured at mixture design set points



	1	2	3	4	5	6	7	8
DRT %	75.50	40.00	40.00	40.00	79.00	72.00	40.00	75.50
PP %	20.00	52.00	59.00	55.50	20.00	20.00	55.50	20.00
Sulphur %	0.50	4.00	0.50	4.00	0.50	4.00	0.50	4.00
TBBS %	4.00	4.00	0.50	0.50	0.50	4.00	4.00	0.50
ZnO %	1.72	1.72	1.72	1.72	1.72	1.72	1.72	1.72
St. A %	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15
TS (MPa)	**5.0 +/-0.3**	**13.7 +/- ***	**12.0 +/-0.4**	**14.8 +/-0.7**	**2.8 +/-0.3**	**4.4 +/-0.1**	**11.4 +/-0.6**	**4.1 +/- 0.1**
EB (%)	**35 +/-4.4**	**6.0 +/- ***	**8.0 +/-1.0**	**6.0 +/-1.1**	**36 +/-7.1**	**22 +/-1.9**	**7.0 +/-0.6**	**22.0+/-2.1**

* Only one reading could be obtained

Table 4.3 Properties measured at center-point replications

	A	B	C
DRT	59.0	59.0	59.0
PP	39.0	39.0	39.0
DCP	1.0	1.0	1.0
S	1.0	1.0	1.0
TS (MPa)	6.6 ±0.3	6.3 ±0.2	6.4 ±0.2
EB (%)	8.0 ±0.6	8.7 ±0.4	9.0 ±0.3

Table 4.4 Overall fit of the quadratic model for TS

	SS	df	MS	F	p
Model	177.5162	7	25.35946	243.1281	0.000400
Total Error	0.3129	3	0.10430		
Lack of Fit	0.2550	1	0.25505	8.8150	0.097187
Pure Error	0.0579	2	0.02893		
Total	177.8292	10	17.78292		

Table 4.5 Overall fit of the quadratic model for EB data

	SS	df	MS	F	p
Model	1312.230	7	187.4614	2351.809	0.000013
Total Error	0.239	3	0.0797		
Lack of Fit	0.074	1	0.0739	0.894	0.444231
Pure Error	0.165	2	0.0826		
Total	1312.469	10	131.2469		

Pareto charts for TS and EB show the various variables and their interactions (Figure 4.2 and Figure 4.3). A Pareto chart is a series of bars, which represent the impact of factors. The factors represented by lengthy bars are more significant than the ones with shorter bars. The factors corresponding to the bars crossing the perpendicular line corresponding to the ‘p’ value of 0.05 may be termed as significant. Thus, from Pareto charts DRT, PP, S and interactions between ‘DRT-PP’ and ‘DRT-S’ seem significant for TS. However, when an interaction term is significant, no conclusions should be drawn about the lower order interaction terms or the individual variables involved in the interaction term. Hence, only ‘DRT- PP’ and ‘DRT- S’ have significant effects on TS and EB. With the same logic, for EB, interactions between ‘DRT- PP’, ‘DRT- S’ and ‘DRT- TBBS’ seem significant.

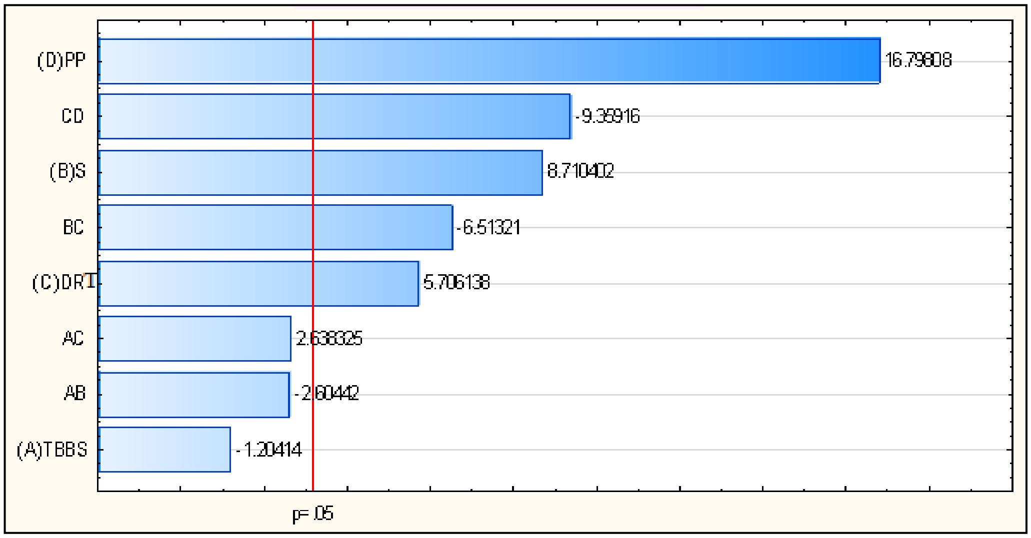


Figure 4.2 Pareto chart for TS

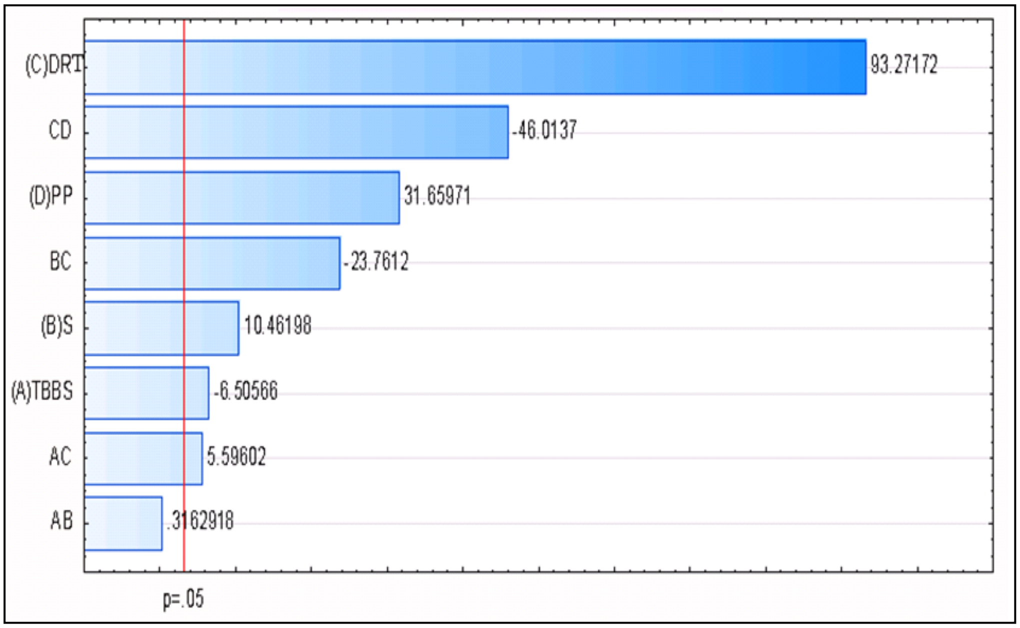


Figure 4.3 Pareto chart for EB

Corresponding model equations for TS and EB are given in Equations 4.1 and 4.2 respectively.

$$\mathbf{TS} = \mathbf{0.060329(DRT)} + \mathbf{0.410288(PP)} + \mathbf{2.058595(S)} - \mathbf{0.28584(TBBS)} - \mathbf{0.006499\ (DRT \times PP)} - \mathbf{0.024000\ (DRT \times S)} + \mathbf{0.009722\ (DRT \times TBBS)} - \mathbf{0.097343\ (TBBS \times S)}$$

…………………………………………………………………………………….........Equation 4.1

$$\mathbf{EB} = \mathbf{0.86205(DRT)} + \mathbf{0.67599(PP)} + \mathbf{2.16147(S)} - \mathbf{1.34408(TBBS)} - \mathbf{0.02793(DRT \times PP)} - \mathbf{0.07654(DRT \times S)} + \mathbf{0.01803(DRT \times TBBS)} + \mathbf{0.01033(TBBS \times S)}$$ … … … … . . … … … ….Equation 4.2

Significant interactions and their corresponding coefficients are highlighted in the model equations. A negative sign indicates that the influence is negative, i.e., an increase in the corresponding interaction term would lead to a decrease in the corresponding property. The significant negative influence of interaction between ‘DRT - PP’ on TS and EB can be taken as a statistical representation of the 'incompatibility' between DRT and PP. The negative influence of 'DRT - S' on both TS and EB, represents that sulphur based dynamic curing does not contribute towards improving properties. The reduction in properties upon addition of sulphur may be attributed to increased incompatibility due to the formation of cured rubber domains, resulting in lesser free chain ends, which led to reduction in mechanical interlocking with the plastic phase. Additionally, 'DRT- TBBS' interaction showed a positive effect on EB, which may be associated with TBBS reacting with residual sulphur in DRT. Predicted values versus observed values for TS and EB are shown to validate the models (Figure 4.4 and Figure 4.5).

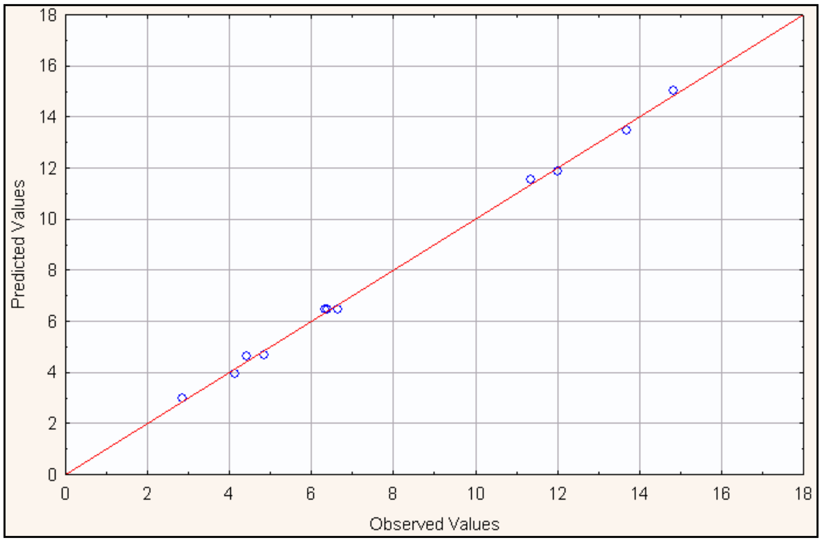


Figure 4.4 Predicted versus observed values for TS

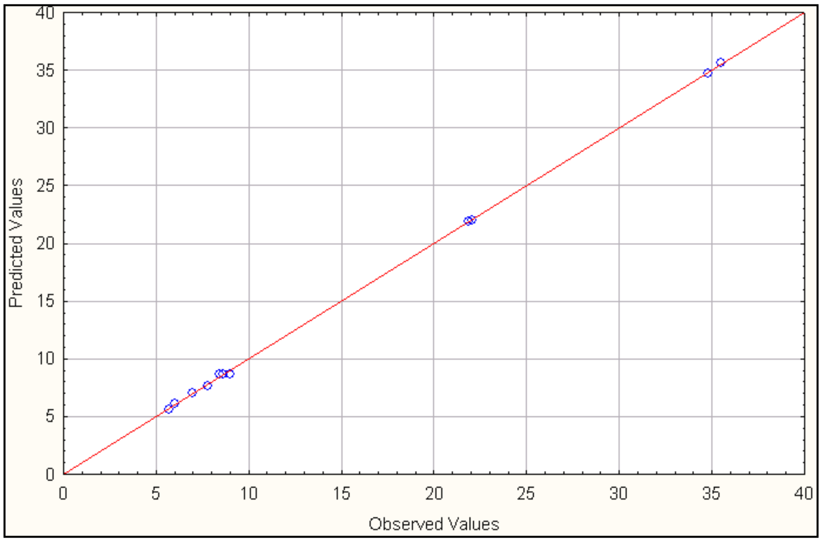


Figure 4.5 Predicted versus observed values for EB

Morphology

SEM pictures of uncured blend of DRT: PP= 60: 40 show distinct bright rubber crumbs and rubber domains (Figure 4.6) in a darker matrix of PP. Bright rubber crumbs suggests that the double bonds in rubber crumbs have not interacted with the matrix phase and hence, the blend is not compatible. As mentioned earlier, these crumbs act as stress-concentrators and result in poor mechanical properties. Upon addition of sulphur, voids appeared and the mechanical properties were deteriorated (Figure 4.7). This may suggest an increased incompatibility upon curing of the rubber phase as suggested by the statistical analysis.

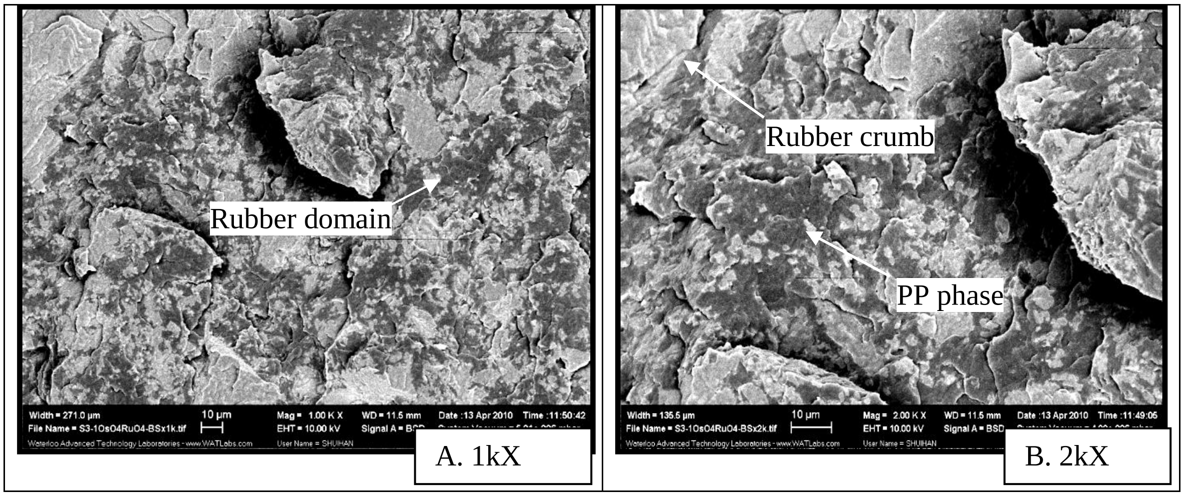


Figure 4.6 DRT: PP= 60:40, Uncured

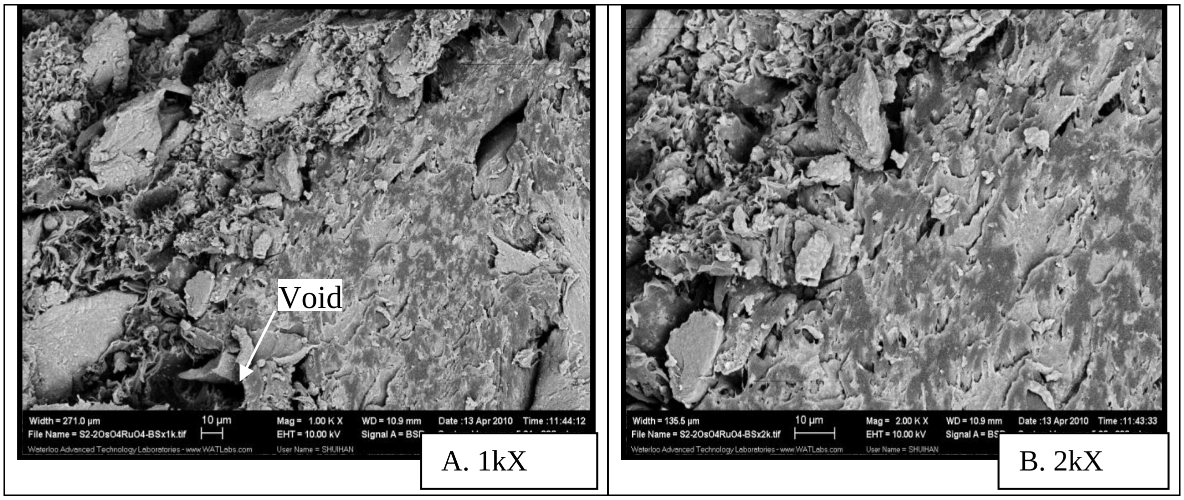


Figure 4.7 DRT: PP= 60:40, sulphur cured

4.3.4 Compatibilizers

Virgin polymers

Experiments were carried out by replacing 10% of DRT by virgin NR, SBR and EPDM one by one in DRT: PP= 60: 40 uncured blends (Figure 4.8). This was carried out to see which of the virgin rubbers helped the most in compatibilizing DRT and PP. None of the additives had any significant positive effect on the mechanical properties. Thus, this approach was not considered in further experiments. This may be due to the presence of rubber crumbs, which acted as stress concentrators and counterweighed the positive effects of incorporation of virgin rubbers.

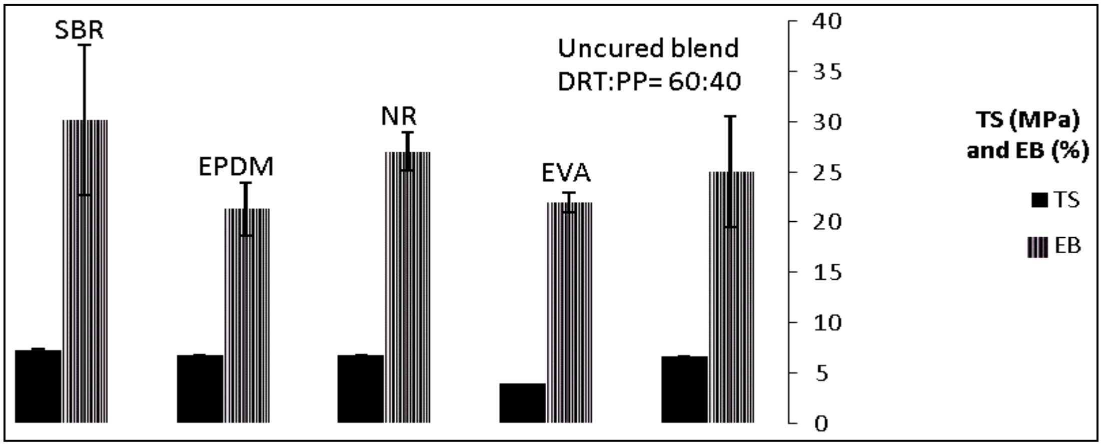


Figure 4.8 Effect of addition of 10% virgin rubbers on TS and EB for DRT/PP blends

Engage® 8480

Engage® 8480 is a specialty resin having a TS of 30 MPa and 1120% EB. As it can be seen (Figure 4.9), an addition of up to 15% of this material led to negligible increase in EB, but the reduction in TS was steeper. As was the case with addition of virgin rubbers, the lack of useful improvement in properties even upon addition of a resin with excellent mechanical properties may be due to the presence of rubber crumbs, which don’t interact with the matrix. Trend lines which were fit to the data are also shown the figure.

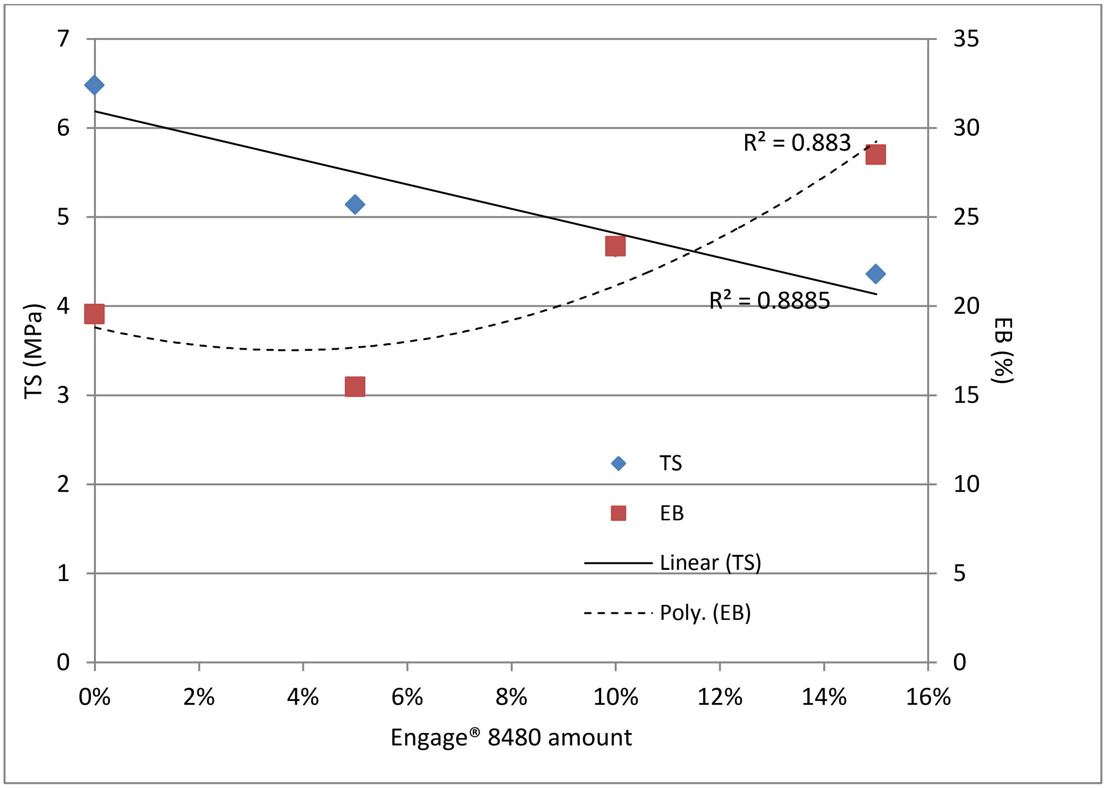


Figure 4.9 Effect of Engage® 8480

Polybond®

Results obtained for 1%, 2% and 5 % addition of Polybond® 3200 to DRT: PP= 60: 40 do not show any significant positive effect on TS and EB (Figure 4.10). Polybond was expected to show some improvement given that it is compatible with PP due to structural similarity and has double bonds to interact with rubber. However, the inertness of rubber crumbs towards any compatibilizer seems the reason behind the absence of an increase in properties.

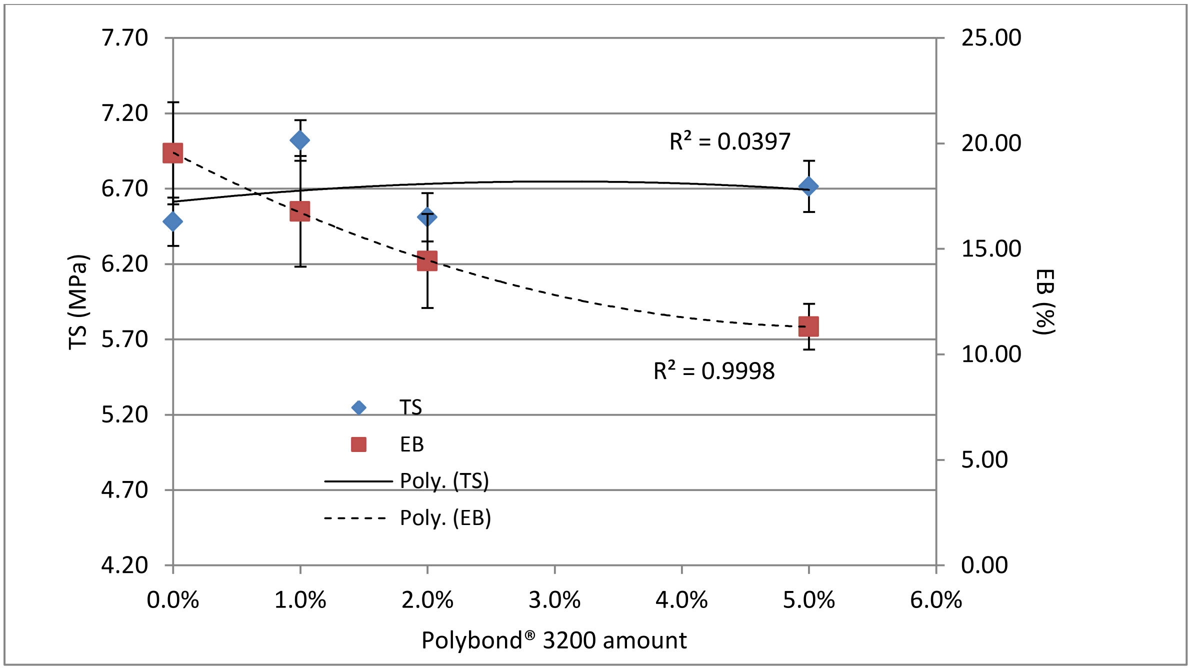


Figure 4.10 Effect of Polybond® 3200

Bitumen

Various approaches were taken to evaluate the effect of bitumen on the TPOs/ TPV samples. Firstly, DRT was pretreated with an equal amount of bitumen (by weight) in a hot vessel (180°C) for a couple of hours. Then the resultant material was mixed with PP keeping the DRT: PP ratio of 60: 40. In another approach, bitumen was added up to 4% and 30% as a part of the total rubber content at the same ratio of DRT: PP= 60: 40. However, in all cases the properties markedly deteriorated.

Ricobond®

Results obtained for 1, 2 and 5 % addition of Ricobond® 1031 do not show a significant positive effect on EB. A little improvement in TS is found at 2% addition (Figure 4.11).

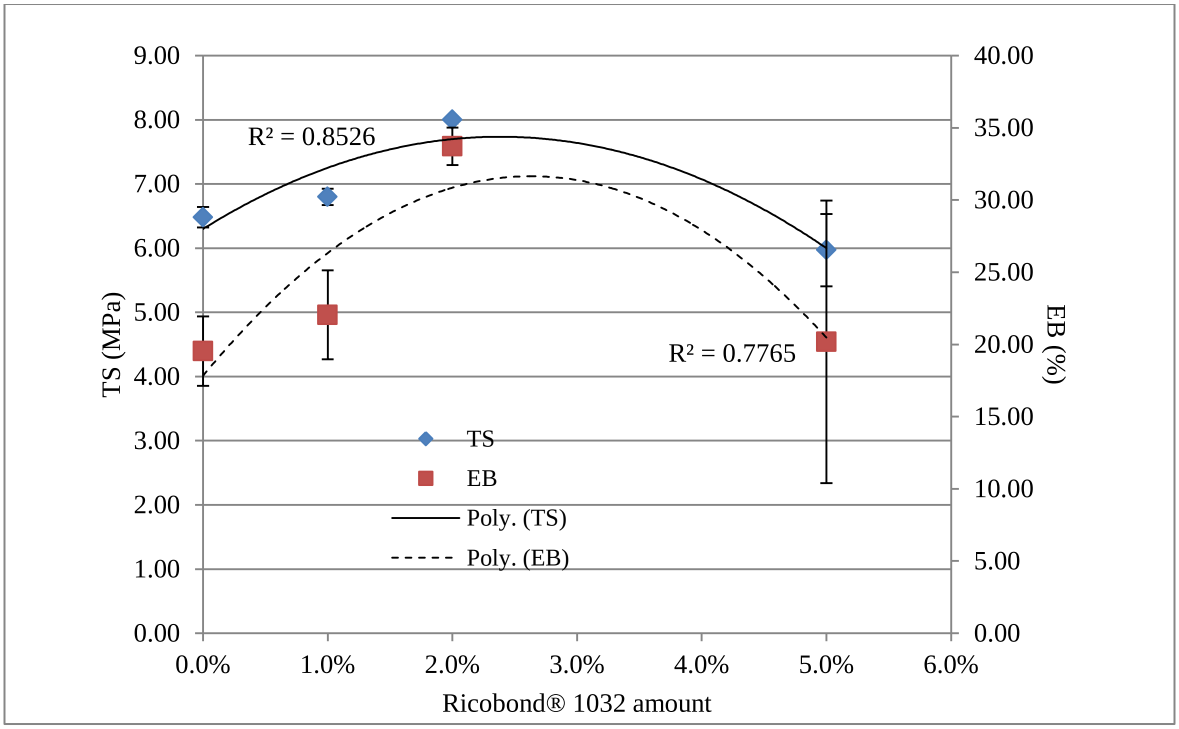


Figure 4.11 Effect of Ricobond® 1031

However, as Ricobond® is a very sticky material, considering the handling issues versus the marginal improvement in properties, it was not pursued further.

Phenolic resin

Phenolic resin, SP-1045 (heat reactive octylphenol-formaldehyde resin, which contains methylol groups) was used to induce reactive compatibilization. However, the phenolic resin did not perform better than the sulphur system (Table 4.6).

Table 4.6 Phenolic resin cure versus sulphur cure for DRT: PP= 60: 40

	(Phr)	**(Phr)**
PP	66.6	93.24
SBR	25	25
DRT	75	75
Sulphur	1.5	-
TBBS	1.5	-
ZnO	3	-
St. A	2	-
SP 1045	-	4
$SnCl_2$	-	1.5
TS (MPa)	6.6 ± 1	6.5 ± 0.1
EB (%)	25 ± 5.5	12 ± 0.4

DCP based cure system

A combination of DCP and sulphur (DCP 3phr and sulphur 2phr) gave significant improvement in properties. The values for TS and EB obtained for DRT: PP= 40:60, 60:40 and 80: 20 were 10 MPa and 7.5%, 9 MPa and 22%, and 6.4 MPa and 37%, respectively. Percent change in properties, when replacing a sulphur cure system by a peroxide/sulphur cure system for three compositions of TPVs (DRT: PP= 40: 60, 60: 40 and 80: 20) were calculated. A positive number indicates an increase in corresponding property, whereas, a negative number indicates a decrease (Figure 4.12).

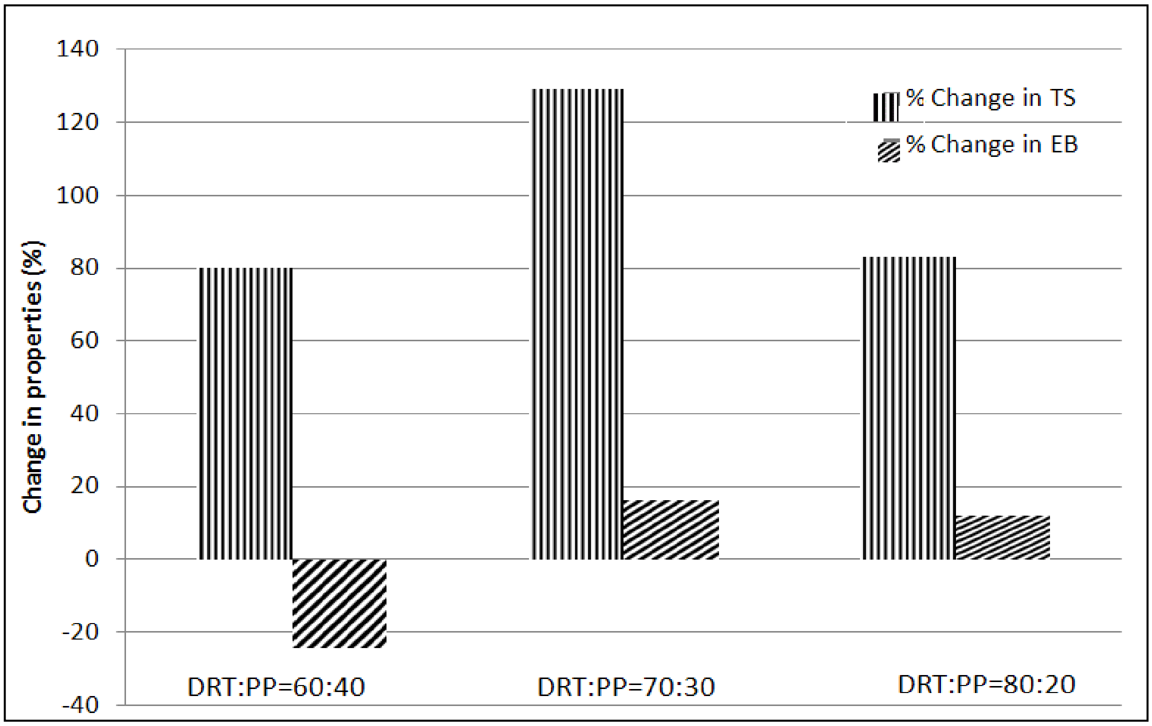


Figure 4.12 Percentage change in TS and EB when using DCP based system (with reference to sulphur based system)

It was observed that peroxide/sulphur curing is relatively more effective when the rubber content is 70-80 %. When the rubber content is 60%, the elongation at break achieved is less than that achieved using sulphur cure, although the increase in TS is greater. This may be due to a crosslinked structure being formed within the PP matrix. However, when the ratio of DRT: PP is 70: 30 and 80: 20, the increase in both TS and EB can be attributed to a better interphase between DRT and PP phases probably caused due to radicals being generated by DCP in both DRT and PP phases. The crumbs might have been involved in reactions with the matrix, leading to a better adhesion to the matrix. This was verified by the SEM pictures of the sample. The contrast between the matrix phase and rubber crumbs was found to be reduced (Figure 4.13). This may be indicating that the double bonds in the rubber crumbs reacted with the matrix leading to improvements in mechanical properties.

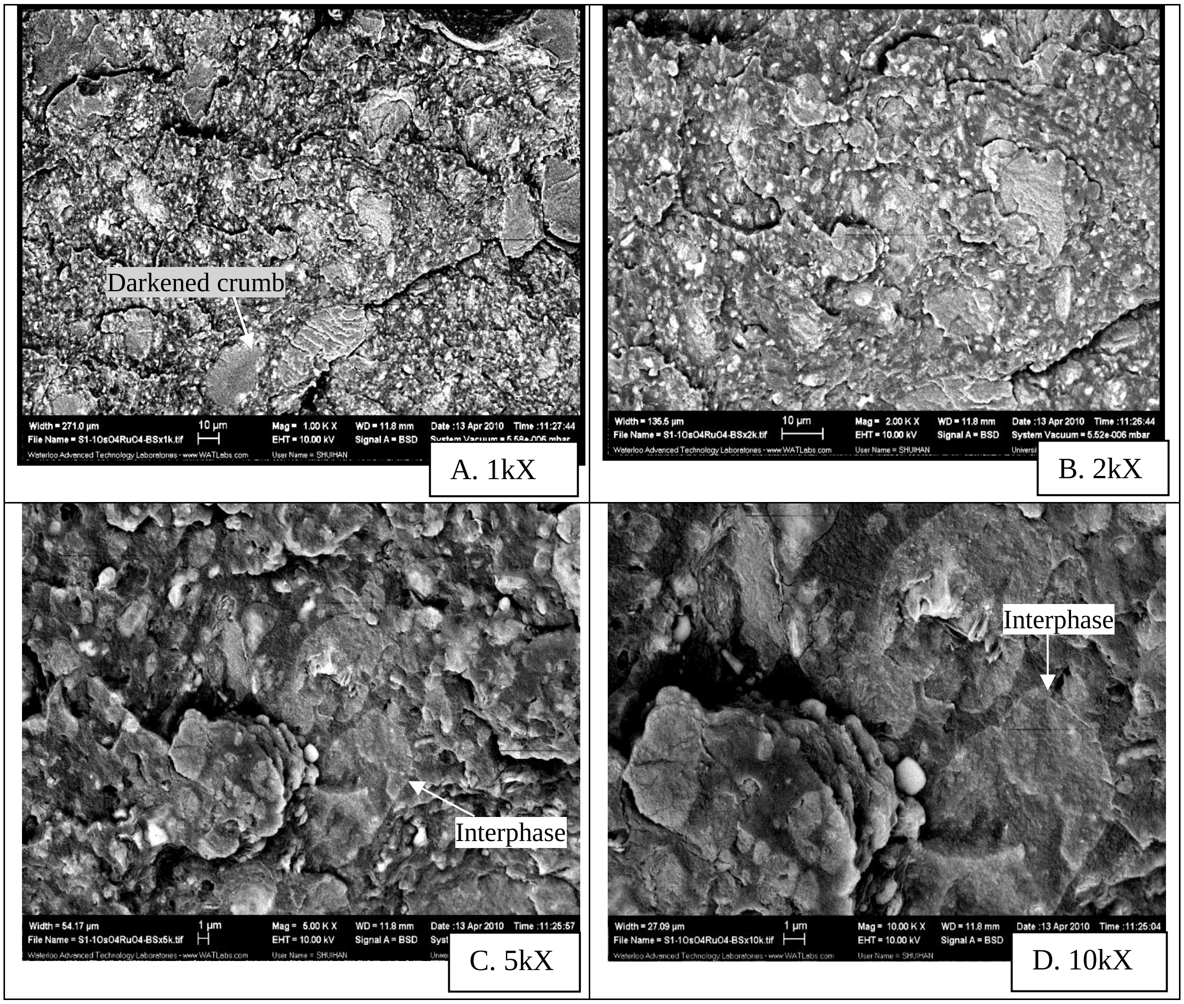


Figure 4.13 DCP/S cured, DRT: PP= 60:40

At 5kX and 10kX magnifications, a thick interphase between crumbs and matrix is visible. These factors may be the reason behind improved properties. Overall, the morphology looked very uniform and well compatibilized.

4.4 Concluding remarks

It is concluded that DRT performs better than CR, and there is a potential to explore the use of DRT in preparation of TPVs. The mixture design approach was helpful to analyze the compatibility between DRT and PP phases, and also to analyze the effectiveness of sulphur based dynamic curing. DRT and PP matrix were found to be mutually incompatible and this was verified by the SEM pictures. Model equations were developed, which can predict the TS and EB for a composition as far as the values of the variables lie within the experimental range. Sulphur dynamic vulcanization was found ineffective in improving the mechanical properties. It was found that most of the commonly used compatibilizers failed to improve the blend properties due to the inertness of rubber crumbs to interact with the matrix. These crumbs therefore, acted as stress concentrators and resulted in poor properties. Out of all the compatibilizers tested, a combination of DCP and sulphur significantly improved the properties. The main reason for the improvement was attributed to involvement of rubber crumbs in reactions with the matrix by DCP radicals, which was verified by analysis of morphology. Further analysis of this curing system seems necessary in order to optimize the dosages of the blend components and understand the underlying mechanism.

CHAPTER 5

STUDY OF DCP/ SULPHUR CURING ON DEVULCANIZED TIRE RUBBER AND POLYPROPYLENE

5.1 Introduction

In the work described in Chapter 4, it was found that a combination of DCP and sulphur resulted in a better compatibilization of devulcanized tire rubber (DRT) and polypropylene (PP). A further investigation of this technique was found necessary so that improvements in the properties could be maximized. Hence, the work described in this section dealt with finding the optimum conditions for using DCP/S system in DRT based TPVs.

DRT contains unsaturated rubbers like NR, synthetic isoprene rubber (IR), butadiene rubber (BR), and SBR, which contain many easily abstractable allylic hydrogen atoms and double bonds that could potentially serve as sites for DCP radical addition. Loan [1] summarized two types of reactions that DCP undergoes in an unsaturated polymer. The first involves hydrogen abstraction by the alkoxy radical derived from the peroxide, followed by pair-wise combination of the resultant polymer radicals to give crosslinks (Figure 5.1). Such a mechanism results in a unit crosslinking efficiency (number of crosslinks formed per molecule of peroxide).

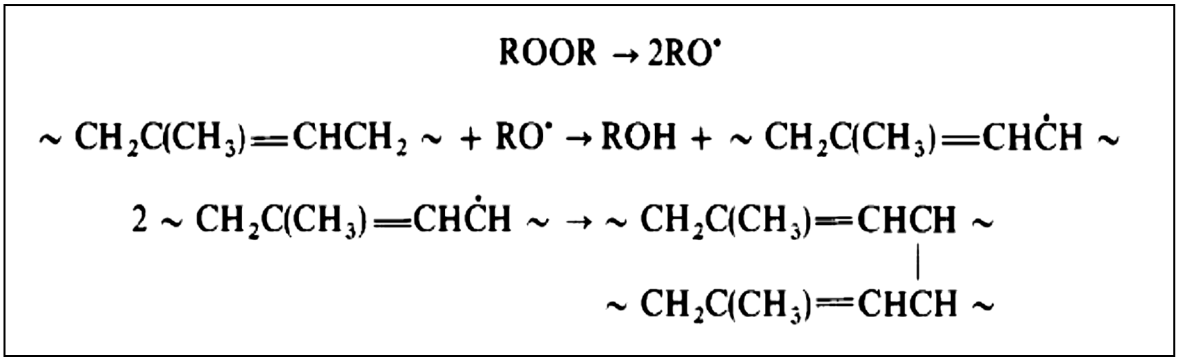


Figure 5.1 Peroxide crosslinking in unsaturated rubber [1]

In the second type (Figure 5.2) of reaction, alkoxy radicals initiate the break-up of the double bonds in the polymer by adding to it (also known as polymerization). The polymerization chain is quite short, but is sufficient to give crosslinking efficiencies well above unity and values of around ten were reported for cis-polybutadiene and SBR. However, this highly efficient reaction, may be inhibited by the presence of molecules that can react with free radicals.

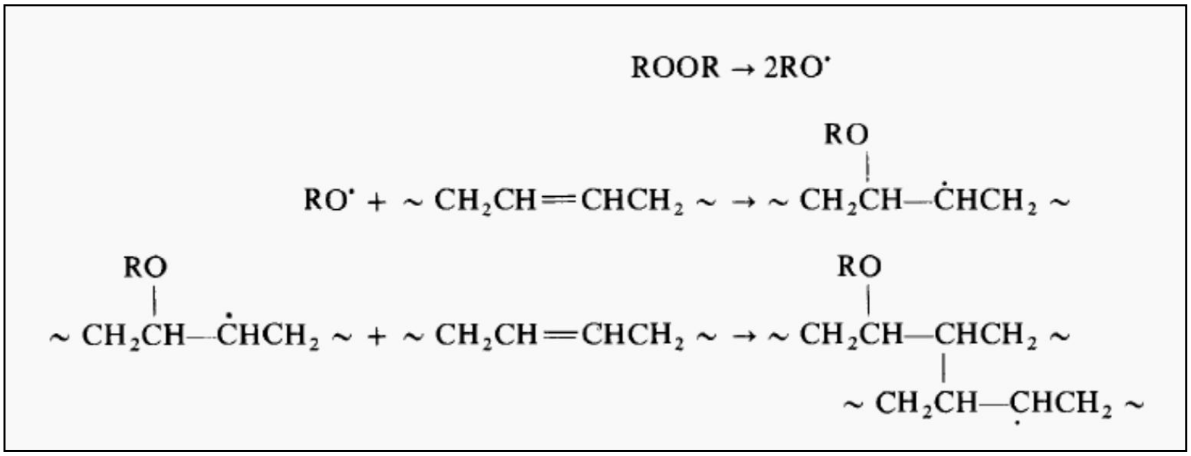
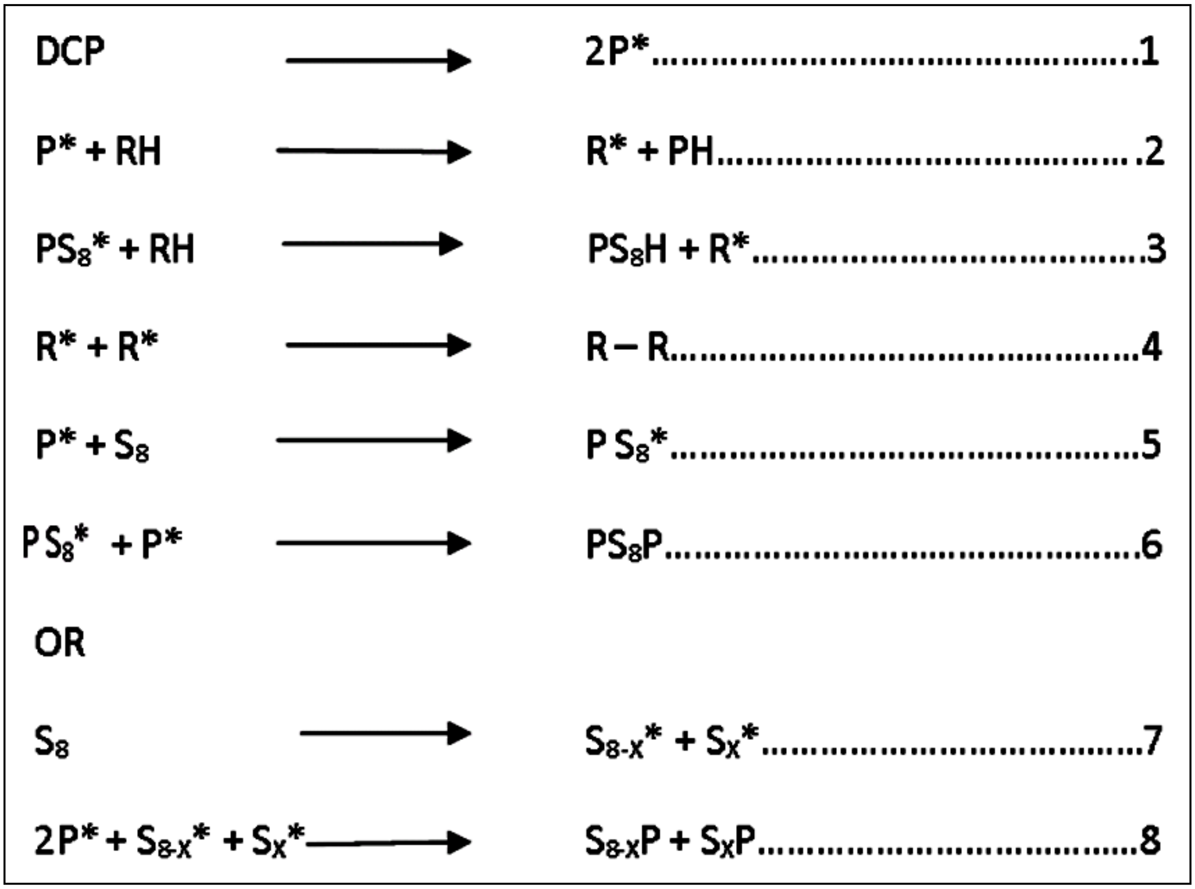


Figure 5.2 Peroxide crosslinking in unsaturated rubber [2]

Due to the high concentration of both of these reactive sites in unsaturated rubbers, it is unclear as to whether peroxide vulcanization of these rubbers follows an abstraction or an addition mechanism. Henning [2] reviewed the use of coagents in the radical curing of elastomers and concluded that the use of coagents in the radical curing of elastomers increased the efficiency of productive radical reactions. Manik and Banerjee [3-5] studied the influence of sulphur in peroxide vulcanization of NR using DCP. Das and Banerjee [6] in a similar work studied the influence of sulphur on DCP vulcanization of SBR. They proposed a mechanism for the reactions that may occur (Figure 5.3).



$$\mathrm{DCP} \longrightarrow 2P^{*} \ldots\ldots 1$$

$$P^{*} + RH \longrightarrow R^{*} + PH \ldots\ldots 2$$

$$PS_8^{*} + RH \longrightarrow PS_8H + R^{*} \ldots\ldots 3$$

$$R^{*} + R^{*} \longrightarrow R - R \ldots\ldots 4$$

$$P^{*} + S_8 \longrightarrow PS_8^{*} \ldots\ldots 5$$

$$PS_8^{*} + P^{*} \longrightarrow PS_8P \ldots\ldots 6$$

OR

$$S_8 \longrightarrow S_{8-x}^{*} + S_x^{*} \ldots\ldots 7$$

$$2P^{*} + S_{8-x}^{*} + S_x^{*} \longrightarrow S_{8-x}P + S_xP \ldots\ldots 8$$

Figure 5.3 Mechanism of DCP/S cure system in SBR [6]

Radicals were believed to be formed through reactions 1, 2 and 3 and crosslinks formed by reaction 4. Reactions 5-6, 7-8 were thought of as the radical destruction steps, out of which 5 and 6 were found to be more prominent.

It is known that the use of DCP with PP causes beta scission of PP chains [7]. This is due to the abstraction of allylic hydrogen by DCP radicals (Figure 5.4). Scholz et al. [8] found that the use of sulphur as a free radical scavenger along with peroxide leads to a radical donor-acceptor reaction that suppresses efficiently the undesired peroxide induced PP chain scission reaction (beta-scission). This results not only in a phase bonding, partially via sulphur bridges, but also directly via C-C bonds. Rado et al. [9] identified PP crosslinked with sulphur -CH_2-S-CH_2- and -CH_2-S-S-CH_2- when using DCP and sulphur. They considered this to be a result of the sulphur being incorporated into the polymer chains.

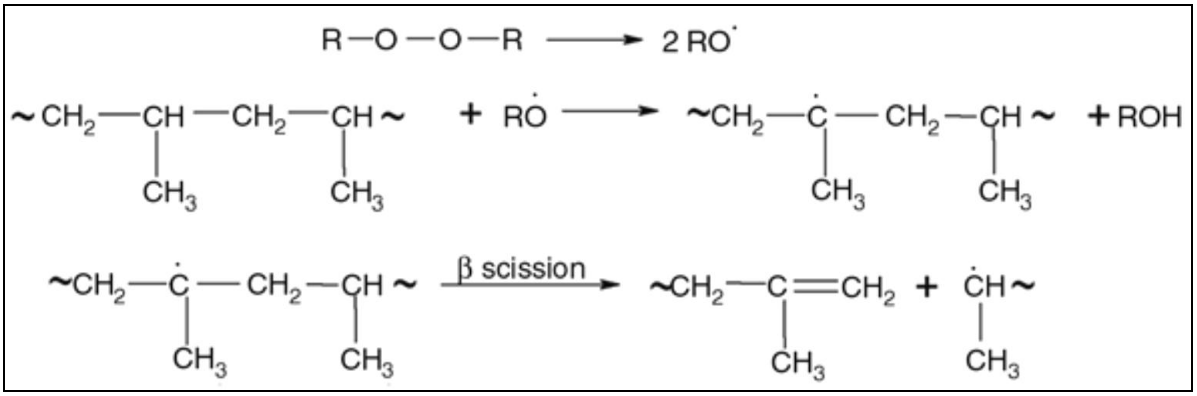


Figure 5.4 Beta scission mechanism [7]

Das [10] reported that addition of small amounts of sulphur as coagent in the peroxide vulcanization of (acrylonitrile butadiene rubber) NBR/ EPDM blends, created coagent bridges, which led to an improvement of certain dynamic and mechanical properties of the vulcanizates. The mechanism suggested by the author is shown in Figure 5.5. It was concluded that sulphur acted as a free radical scavenger in the peroxide vulcanization of NBR/ EPDM blends and stabilized the tertiary radicals formed from the PP units, thus restricting the main chain scission and improving the physical properties.

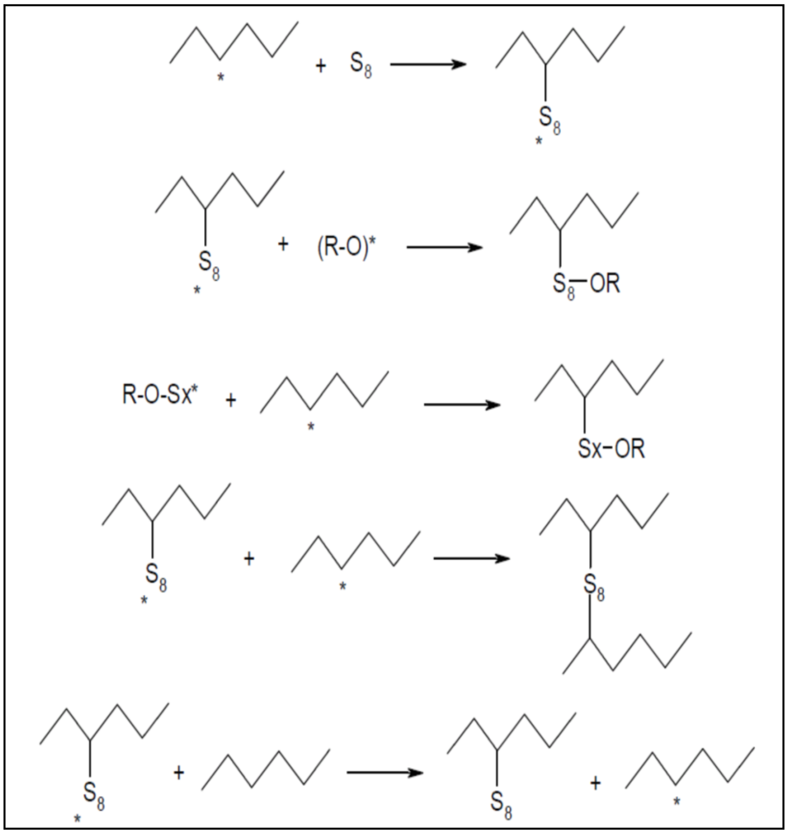


Figure 5.5 Mechanism of peroxide vulcanization in the presence of sulphur [10]

Thitithammawong et al. [11] studied the influence of sulfur/ peroxide vulcanization systems on the mechanical and thermal properties of NR/ PP blends. They found that the TPV had a high crosslink density with a combination of crosslink patterns from sulfur linkages and C–C linkages, and a low level of competing reactions from the peroxide causing

PP degradation. As a result, improvements in the mechanical and thermal properties were obtained.

Based on this information, it is proposed that sulphur may be involved in three main types of reactions in our system. Foremost, sulphur may form crosslinks between rubber-rubber chains due to unsaturation present in the rubber molecules. Secondly, it can react with DCP radicals forming ROS, ROOS or ROSOR (R being the hydrocarbon group of the radicals produced from the DCP and O indicating the oxygen of the peroxide), and thus act as radical scavenger for the peroxide radicals. This may lead to a reduction in reactive compatibilization efficiency of peroxide, and hence deteriorate the properties. Thirdly, it can react and stabilize the tertiary radicals on PP molecules created by abstraction of allylic hydrogen by DCP radicals. Thus, by avoiding beta-scission degradation, and forming sulphur crosslinks ($-CH_2-S-CH_2-$ and $-CH_2-S-S-CH_2-$), a better compatibility may be achieved. Although all the reactions may occur simultaneously, it is necessary to analyze if certain factors affect the relative prominence of one type of reaction over others. A detailed study in this regard has not been carried out yet. The knowledge of ideal conditions can be applied to adjust the DCP/ S ratio in order to get the optimum properties of the blends.

5.2 Experimental

5.2.1 Materials

The PP (PP31KK01, MFR= 5g/min) used had a TS of 24 MPa and an EB of 7%. The DRT used had a TS of 8.9 MPa and an EB of 172%, when cured with standard sulphur based package (S=1.5, TBBS=1.5, ZnO=3, St. A=2 phr). The curing package used for dynamic vulcanization consisted of DCP and sulphur either individually or in combination.

5.2.2 Experimental Design

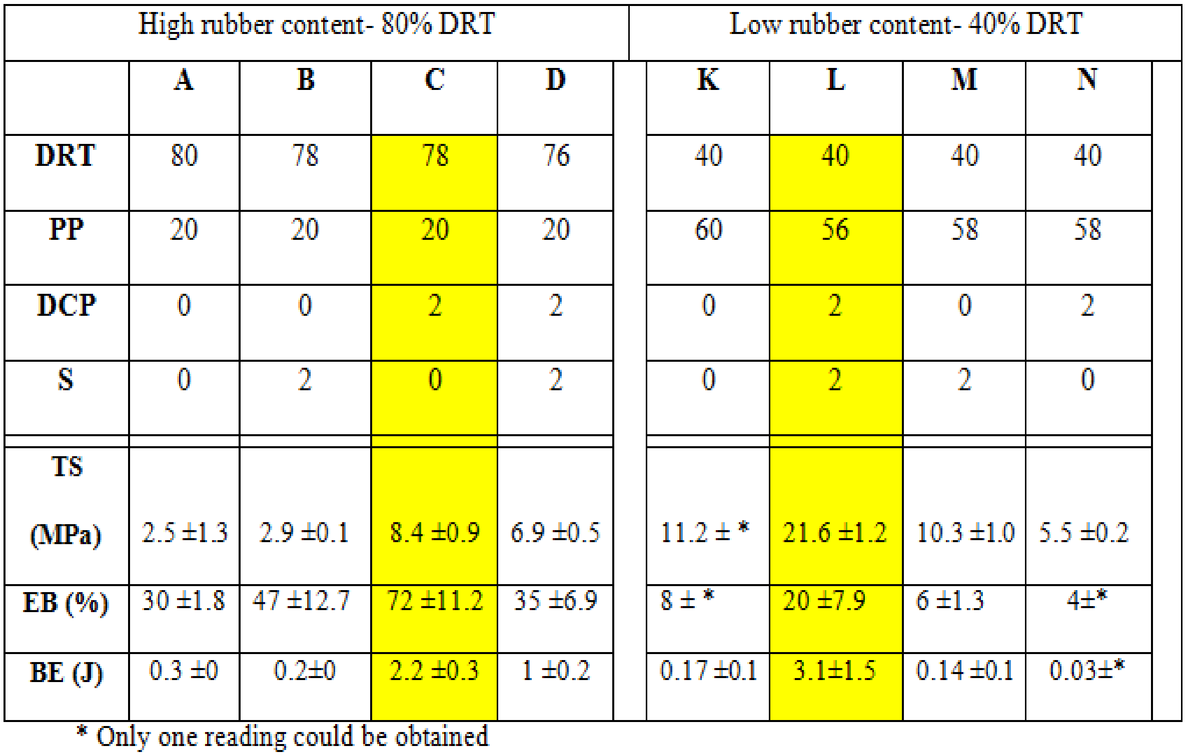
The present work adapted a mixture design of experiments to analyze the influence of dosages of devulcanized rubber produced from tire rubber (DRT), polypropylene (PP), dicumyl peroxide (DCP) and sulphur (S) on the key mechanical properties namely tensile strength (TS) and elongation at break (EB) of the blends. The ranges chosen to test DCP and sulphur were 0%- 2%, for PP 20%- 60% and for DRT 40%- 80%. Three center-point replications were carried out to calculate pure error and LOF (lack of fit) terms for the models. Mixing was carried out in a Haake batch mixer at conditions that were mentioned in Chapter 3.

5.3 Results and Discussion

5.3.1 Mechanical properties

TS, EB and breaking energy (BE) results for the experiments are shown in Table 5.1 and Table 5.2. It was observed that when the DRT content was high (approximately 80%), use of only DCP as a curing agent resulted in a material with good properties (an increase of 236% in TS, 100% in EB and 633% in BE compared to uncured blend). On the other hand, at a lower DRT content (approximately 40% rubber), the combination of DCP and sulphur produced better results (an increase of 90% increase in TS, 150% in EB and 1724% in BE). The probable reasons for these results are discussed later in the chapter.

Table 5.1 Properties measured at mixture design set points



	High rubber content- 80% DRT				Low rubber content- 40% DRT			
	A	**B**	**C**	**D**	**K**	**L**	**M**	**N**
DRT	80	78	78	76	40	40	40	40
PP	20	20	20	20	60	56	58	58
DCP	0	0	2	2	0	2	0	2
S	0	2	0	2	0	2	2	0
TS (MPa)	2.5 ±1.3	2.9 ±0.1	8.4 ±0.9	6.9 ±0.5	11.2 ± *	21.6 ±1.2	10.3 ±1.0	5.5 ±0.2
EB (%)	30 ±1.8	47 ±12.7	72 ±11.2	35 ±6.9	8 ± *	20 ±7.9	6 ±1.3	4±*
BE (J)	0.3 ±0	0.2±0	2.2 ±0.3	1 ±0.2	0.17 ±0.1	3.1±1.5	0.14 ±0.1	0.03±*

* Only one reading could be obtained

Table 5.2 Properties measured at center-point replications

	1	**2**	**3**
DRT	59.0	59.0	59.0
PP	39.0	39.0	39.0
DCP	1.0	1.0	1.0
S	1.0	1.0	1.0
TS (MPa)	6.1 ±0.3	9.0 ±0.6	11.0 ±0.3
EB (%)	11 ±3.0	15 ±3.3	21 ±1.0
BE (J)	0.2 ±0.1	0.5±0.1	0.9 ±0.1

The high variance in the TS values of the centre-point replications is thought to be caused due to the presence of non-uniform rubber crumbs. Analysis of the results using Statistica software revealed the significant variables, which influenced the dependent factors (TS and EB). Linear and quadratic models could not be fitted to the data as the LOF term was found to be significant. However, cubic models were successfully fitted to the data for TS and EB (Table 5.3 and Table 5.4).

Table 5.3 Overall fit for cubic model (TS)

	SS	**df**	**MS**	**F**	**p**
Model	258.7163	6	43.11939	13.12611	0.013130
Total Error	13.1400	4	3.28501		
Lack of Fit	1.0000	2	0.50002	0.08238	0.923894
Pure Error	12.1400	2	6.07000		
Total	271.8564	10	27.18564		

Table 5.4 Overall fit for cubic model (EB)

	SS	df	MS	F	p
Model	4088.599	7	584.0856	10.72816	0.038592
Total Error	163.332	3	54.4441		
Lack of Fit	109.479	1	109.4791	4.06583	0.181291
Pure Error	53.853	2	26.9266		
Total	4251.931	10	425.1931		

As seen in Pareto charts (Figure 5.6 and Figure 5.7), both TS and EB are positively influenced by the interaction between PP, DCP and sulphur (‘PP-DCP-S’). This may be considered as a reflection of the stabilizing action of sulphur to prevent beta-scission of PP chains. Additionally, EB is negatively influenced by the interaction between ‘DRT- PP’, which may be interpreted as incompatibility between the phases. There is a positive influence of interaction between ‘DRT- DCP’ on EB, which may be associated with curing of the DRT phase by peroxide radicals.

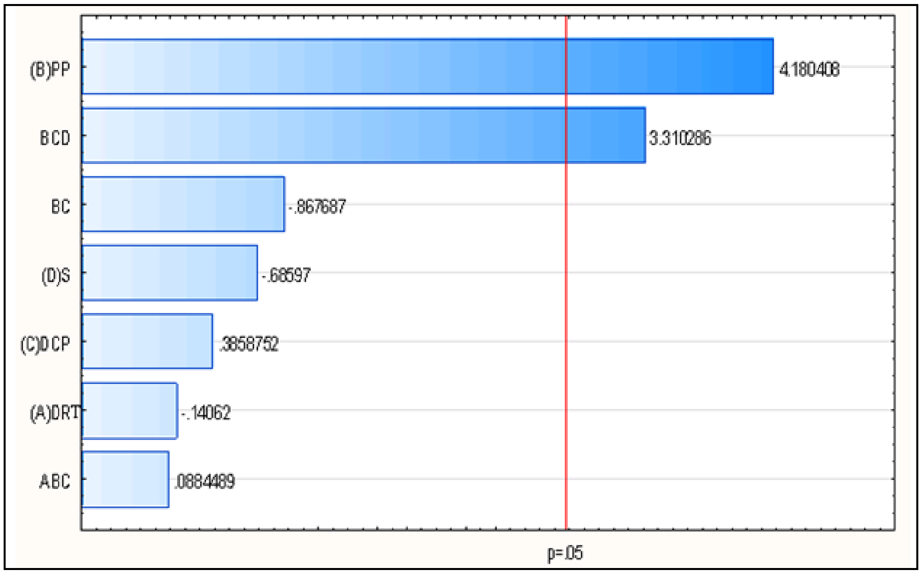


Figure 5.6 Pareto chart for TS

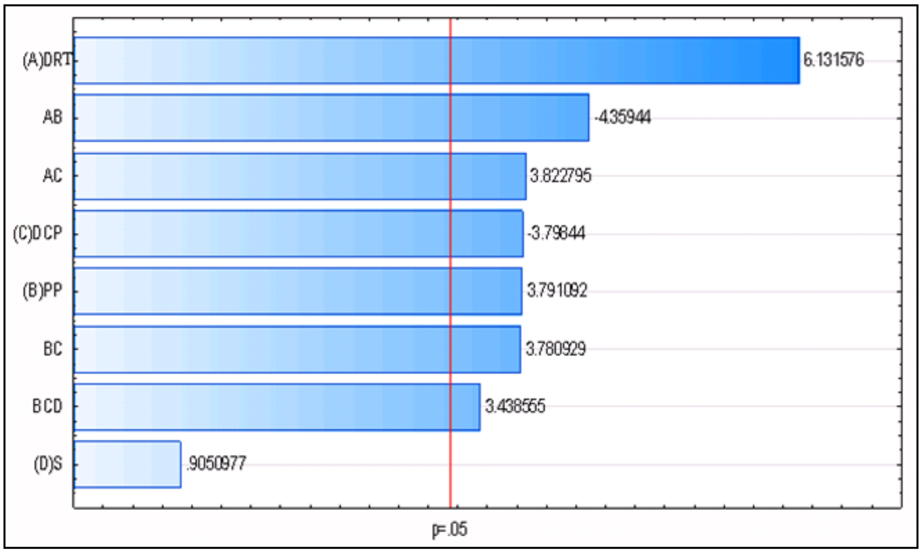


Figure 5.7 Pareto chart for EB

The coefficients obtained for the various interactions were used to form model equations (Equations 5.1 and 5.2), which can be used to predict the dependent variable for any given composition as long as the values (in percentage) for the independent variables lie within the range chosen for the experiment. Significant interaction terms and their corresponding coefficients are highlighted in the model equations.

$\mathbf{TS} = -\mathbf{0.0049}(\mathbf{DRT}) + \mathbf{0.199457}(\mathbf{PP}) + \mathbf{2.369333}(\mathbf{DCP}) - \mathbf{0.883249}(\mathbf{S}) - \mathbf{0.101662}(\mathbf{PP} - \mathbf{DCP}) - \mathbf{0.000444}(\mathbf{DRT} - \mathbf{DCP}) + \mathbf{0.071527}(\mathbf{PP} - \mathbf{DCP} - \mathbf{S})$……………………….....................Equation 5.1

$\mathbf{EB} = \mathbf{1.506}(\mathbf{DRT}) + \mathbf{2.3500}(\mathbf{PP}) - \mathbf{1711.56}(\mathbf{DCP}) + \mathbf{3.2713}(\mathbf{S}) - \mathbf{0.0827}(\mathbf{DRT} - \mathbf{PP}) + \mathbf{17.75}(\mathbf{DRT} - \mathbf{DCP}) + \mathbf{17.261}\ (\mathbf{PP} - \mathbf{DCP}) + \mathbf{0.343}\ (\mathbf{PP} - \mathbf{DCP} - \mathbf{S})$ … …. . … … … … ….Equation 5.2

The proposed models were validated using a plot of predicted versus observed values (Figure 5.8 and Figure 5.9).

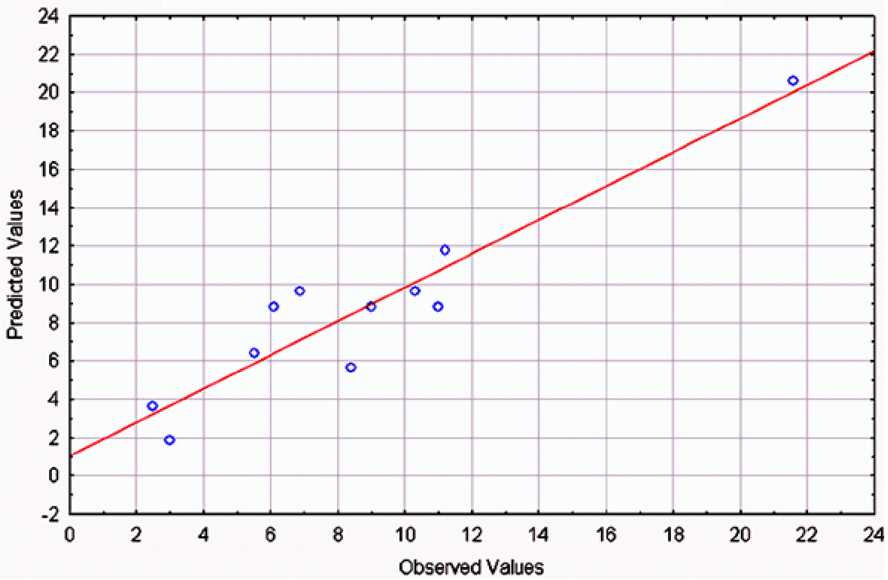


Figure 5.8 Predicted versus observed values (TS)

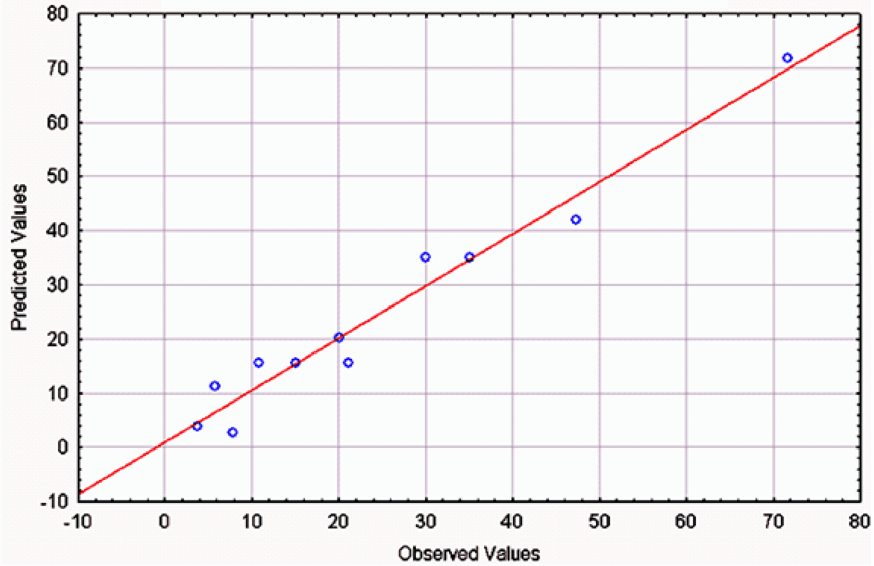


Figure 5.9 Predicted versus observed values (EB)

5.3.2 Morphology

Samples A, B, C, D (DRT: PP= 80: 20 approximately)

SEM pictures were taken at 200X and 1kX magnifications for all the samples (Figure 5.10 and Figure 5.11). The differences in samples are easily visible in 200X images. Sample A (uncured blend) shows large particles of crumb rubber (indicated by bright regions) and voids, due to which the mechanical properties of the materials were found to be inferior. Bright regions of crumb rubber indicate that they did not compatibilize with the matrix. Upon addition of sulphur, i.e., sample B, the edges of rubber crumbs looked smoothened out and darkened in contrast, suggesting that sulphur induced some degree of crosslinking in the rubber crumbs. However, the interphase may not have strengthened, and hence, the mechanical properties remained similar to the uncured sample. When DCP was added (sample C), bright rubber crumbs, which appeared in the uncured sample, darkened in a significant manner. As there is an accompanying increase in properties too, this may be an indication that the double bonds of the crumbs were involved in reactions with the matrix, which resulted in improved interfacial adhesion.

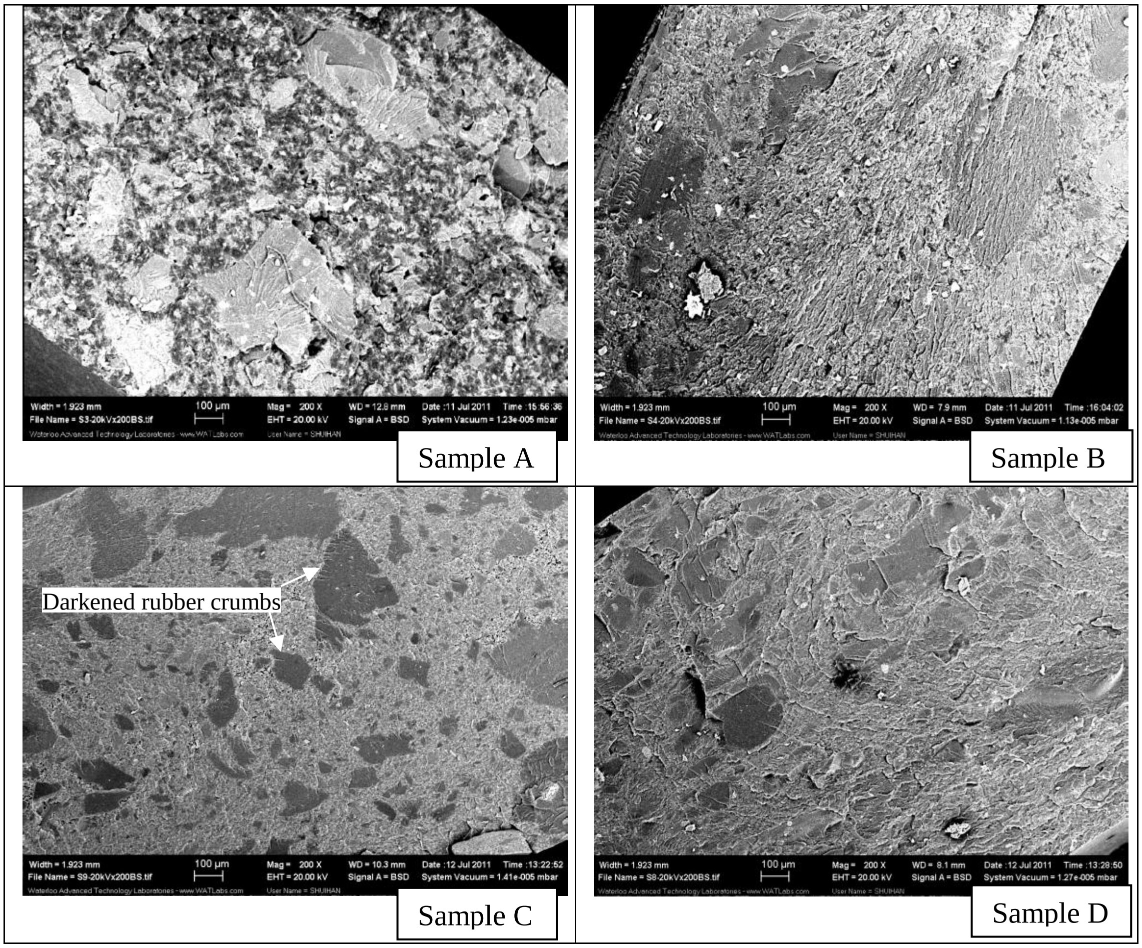


Figure 5.10 SEM images of the samples A, B, C, D at 200X magnification

Hence, it seems that the DCP generated radicals on crumb rubber and PP too and led to interfacial reactions between PP and rubber phase, along with crosslinking reactions within the rubber phase itself. Intuitively, one would think that DCP radicals would degrade PP, but it appears that due to the scarce presence of PP in the composition, the degradation reactions were not dominant. Also, as we were using a PP with high MFI, little degradation may not severely deteriorate the properties.

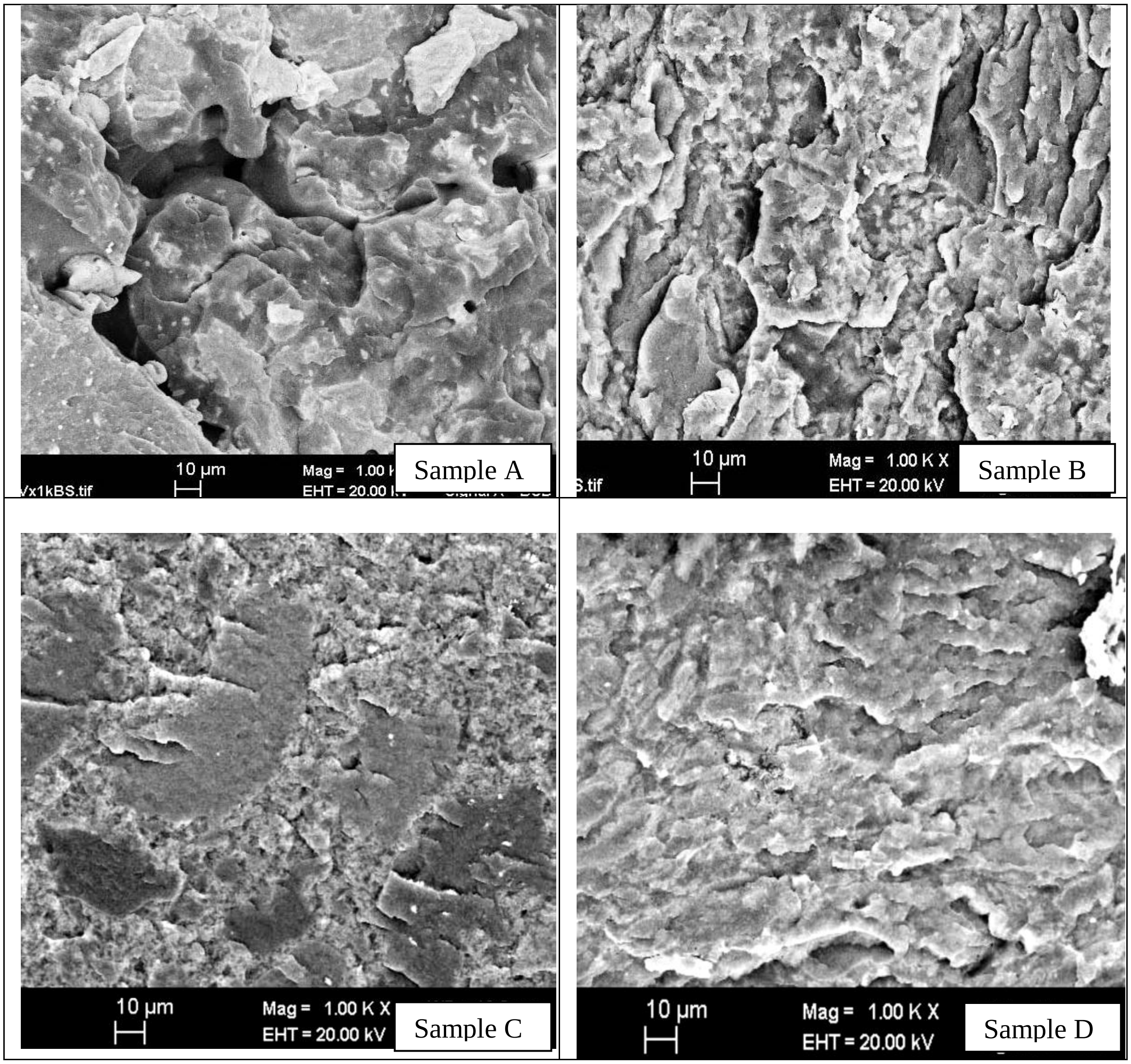


Figure 5.11 SEM images of the samples A, B, C, D at 1kX magnification

SEM pictures for sample C were taken at 5kX and 10 kX (Figure 5.12). The darkened rubber crumbs seem adhering well with the matrix as there is no evidence of phase separation or presence of voids.

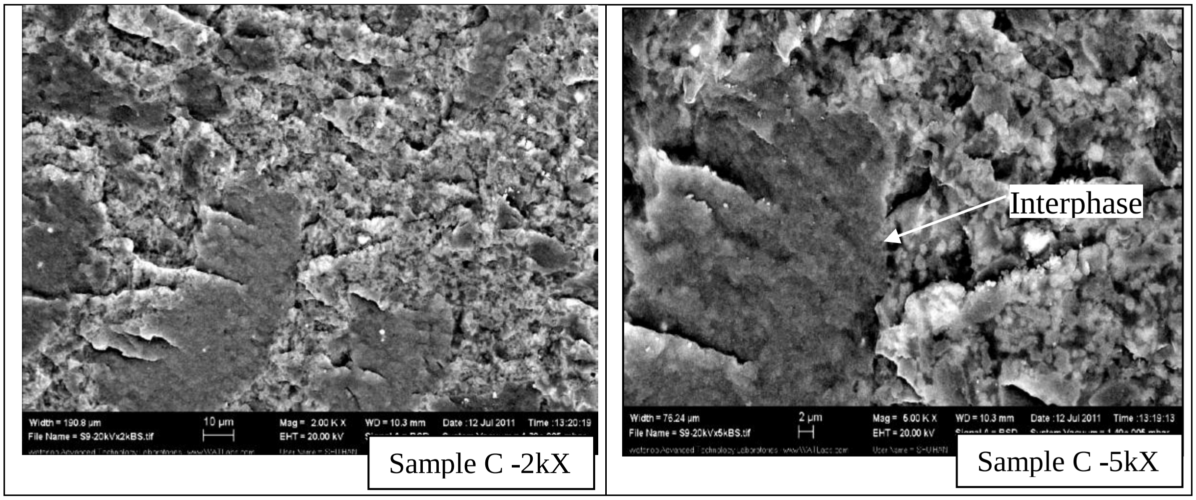
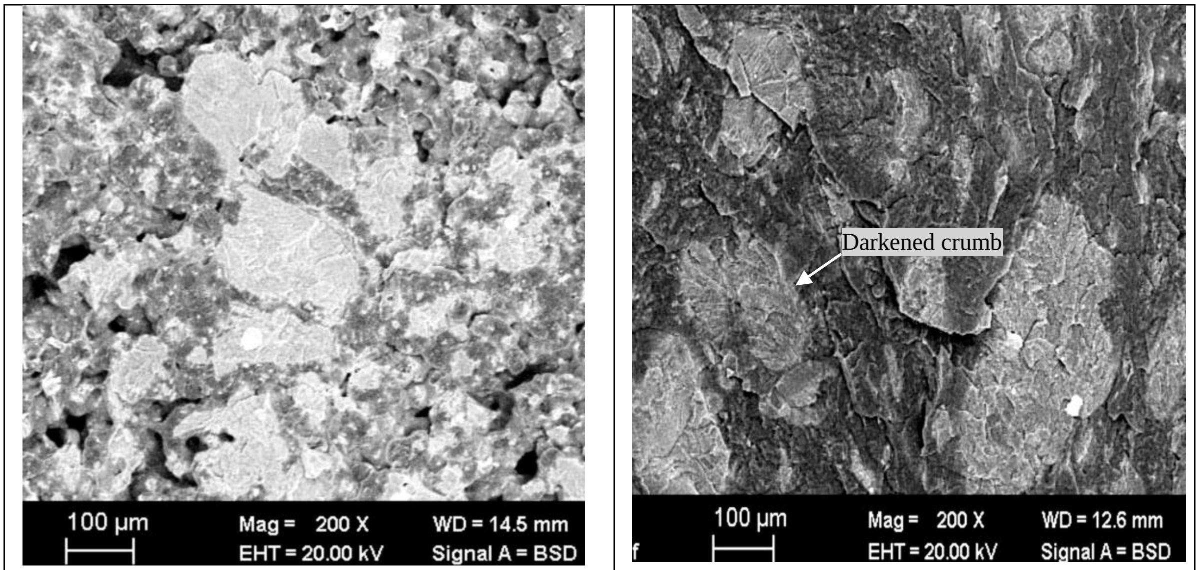


Figure 5.12 Sample C at 2kX and 5kX magnification

In sample D, when sulphur was added along with DCP, the blend showed inferior mechanical properties to the DCP cured material (sample C). The morphology of sample D, however, looked similar to that of sample C. It should be noted that sample D performed better than uncured and sulphur cured samples (A and B), and hence it seems to be better compatibilized than samples A and B. The possibility for such results may be due to the presence of sulphur, which may have acted as radical scavenger for some of the DCP radicals and also competed for rubber unsaturation sites, in turn reducing the efficiency of the DCP radicals to cause interfacial reactions.

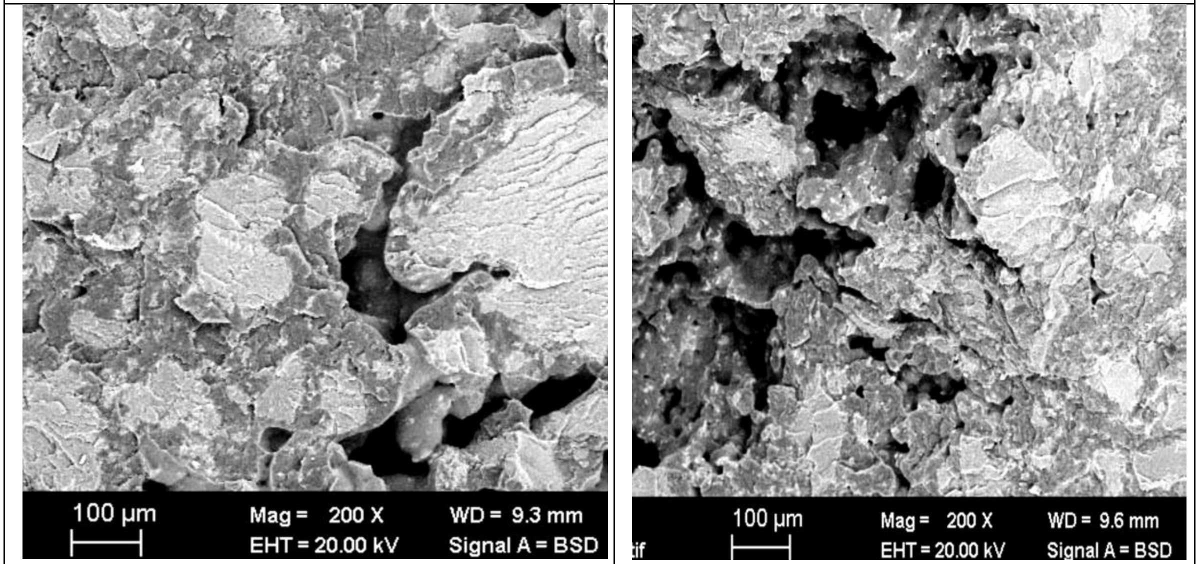
<u>Samples K, L, M, N</u> (DRT: PP= 40: 60 approximately)

SEM images of samples with low DRT content (K, L, M, N) were taken at 200X and 1kX magnification (Figure 5.13 and Figure 5.14**)**. The uncured blend of the DRT and PP (sample K) showed a lot of voids and bright rubber crumbs. This indicates incompatibility between the phases and accordingly, the material showed relatively poor properties. Upon addition of sulphur (sample M), no major changes in the morphology were observed. In case of sample N, when only peroxide was added, the morphology remained the same; however, there was a fall in the mechanical properties. This is probably due to beta-scission degradation of the PP phase, which cannot be seen in SEM images. However in sample L, where sulphur was added along with the DCP, the properties of the material almost doubled up with reference to the uncured blend. The morphology does not show presence of any voids and is accompanied with darkening of the rubber crumbs. This may suggest a good interaction of the rubber crumbs with the matrix, which resulted in the improved properties.



Sample K

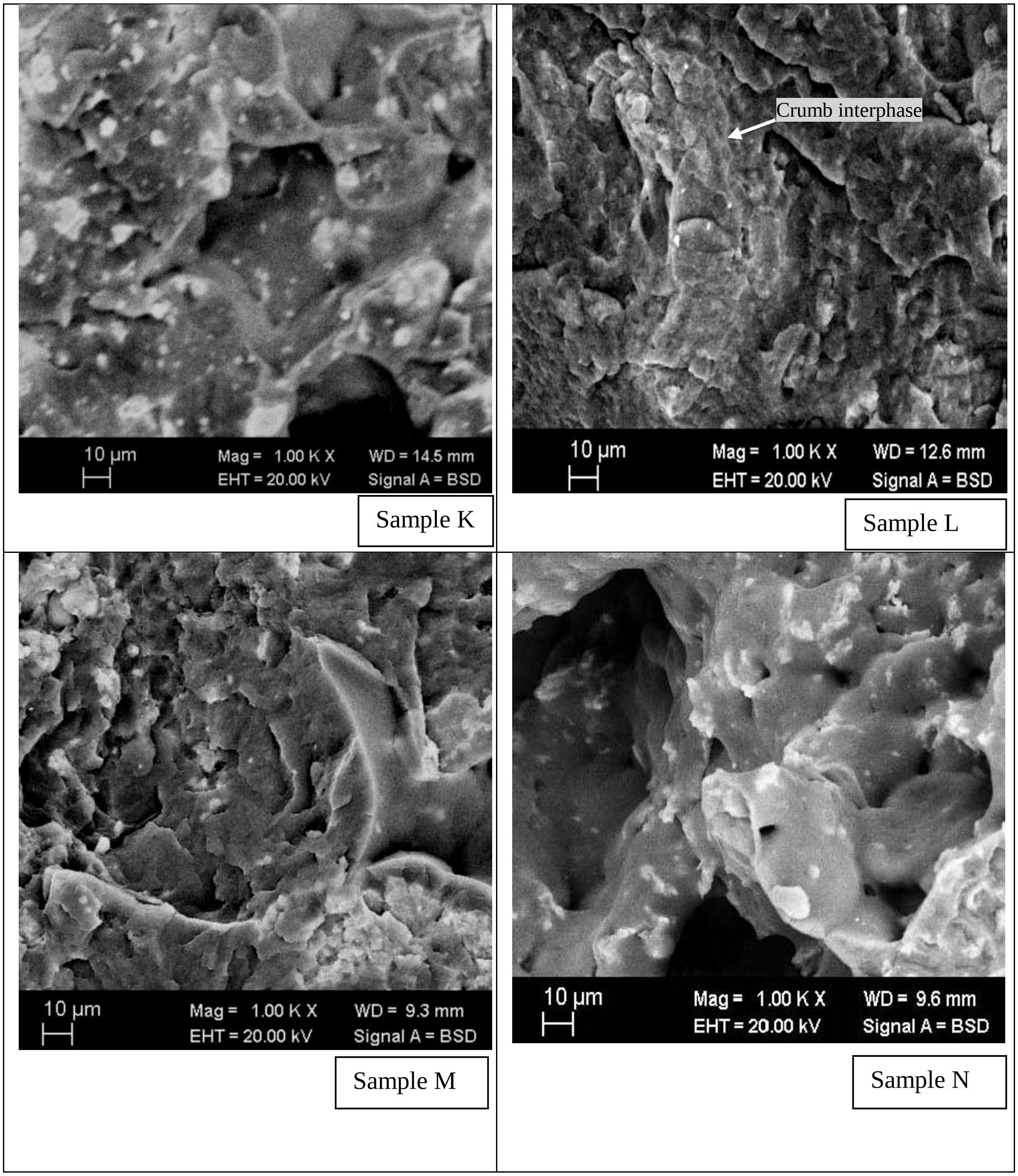
Sample L



Sample M

Sample N

Figure 5.13 SEM images of the samples K, L, M, N at 200X magnification



Sample K

Sample L

Sample M

Sample N

Figure 5.14 SEM images of the samples K, L, M, N at 1kX magnification

The morphology of sample L looks very uniform and intimate, as there are no highly contrasting regions visible even at 5kX (Figure 5.15). The improvement in morphology and properties is attributed to the presence of sulphur, which prevented PP degradation by preferably reacting with the tertiary radicals and stabilizing them, whereas, the reactions between the rubber phase and plastic phase continued to form the interphase resulting from the C-C bonds and also C-S-C sulphur bridges. This phenomenon may be the reason behind the significant positive influence of ‘PP-DCP-S’ on TS and EB as found in the statistical analysis.

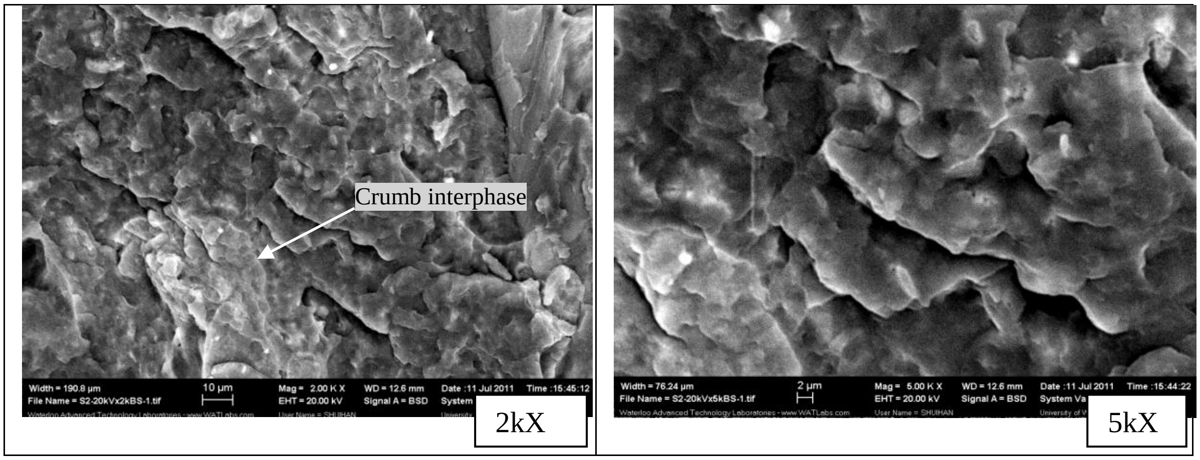


Figure 5.15 SEM images of the sample L at 2kX and 5kX magnification

5.3.3 Thermal Studies

DSC Analysis

Samples A, B, C, D **(**DRT: PP= 80: 20 approximately): Degree of crystallinity and melting point (MP) of samples were obtained from DSC analysis (Table 5.5). Figure 5.16 shows the corresponding plots of heat flow versus temperature. Three replications of the centre-point sample yielded a standard deviation of 3.5 units for the degree of crystallinity and 1.2 units for the melting temperature.

Table 5.5 Melting point and degree of crystallinity for blends with high rubber content

	Sample A (Uncured)	**Sample B (Only sulphur)**	**Sample C (Only DCP)**	**Sample D (Sulphur+ DCP)**
TS (MPa)	2.5 ± 1.3	2.9 ± 0.08	8.4 ± 0.9	6.9 ± 0.5
EB (%)	30 ± 1.8	47.3 ± 12.7	72 ± 11.2	35 ± 7
Melting point (°C)	168.2	168.2	106.2	167
% Degree of Crystallinity	44.9	30.3	2.5	38.6

It is seen that sample C, which showed better properties, displayed a significant drop in the degree of crystallinity and MP, when compared to the uncured blend. An increase in interaction between the phases is known to retard the formation of crystallites by restricting the mobility of the molecules. In other words, compatibilization leads to a reduction in the degree of crystallinity and melting temperature, hence, the results support the assumption that sample C is well compatibilized. Due to the same reason, samples B and D also show a reduction in the degree of crystallinity, although not as significant as sample C.

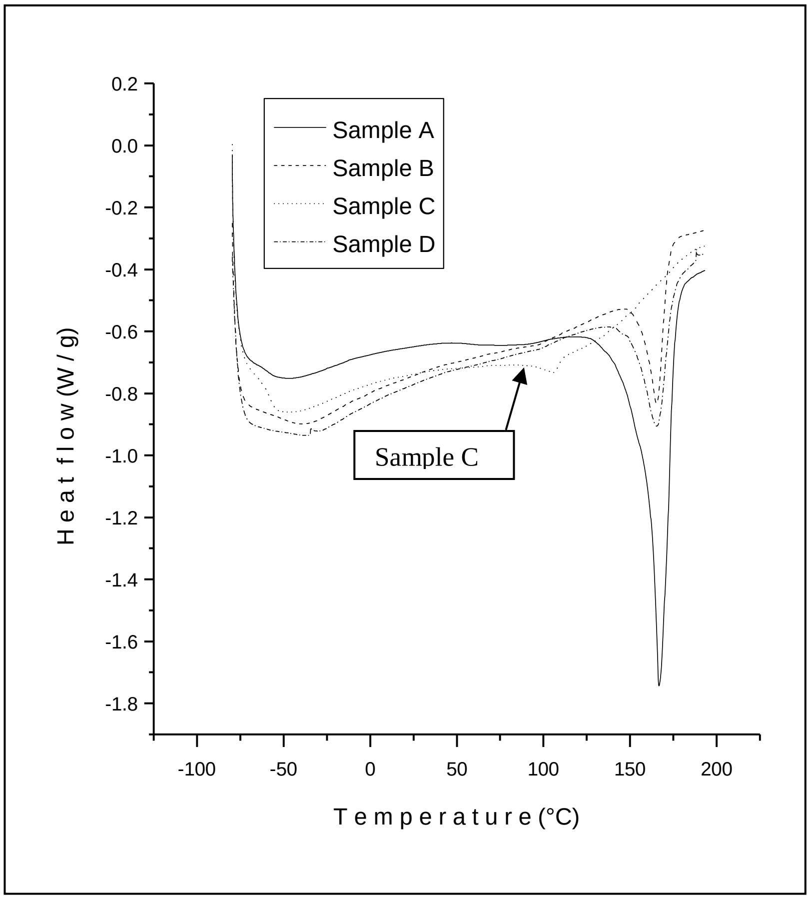


Figure 5.16 DSC plots for samples A, B, C, D

Samples K, L, M, N (DRT: PP= 40: 60 approximately): For blends with low rubber concentration (Table 5.6), sample L, which showed better properties, indicated a decrease in the MP and degree of crystallinity. Sample M also showed similar trend, which suggests that sulphur cured rubber domains may have affected the kind of crystallites formed. It was visibly noted that sample N was degraded during melt mixing. Thus, the reduction in the degree of crystallinity in sample N could be associated to degradation effects. Degradation leads to shorter chains, which makes chain folding and alignment difficult and hence, retards crystallite formation. Figure 5.17 shows the corresponding DSC plots.

Table 5.6 Melting point and degree of crystallinity for blends with high plastic content

	Sample K (Uncured)	**Sample L (DCP+S)**	**Sample M (Only Sulphur)**	**Sample N (Only DCP)**
TS (MPa)	11.2 ± *	21.6 ± 1.2	10.3 ± 1.0	5.5 ± 0.2
EB (%)	8 ± *	20 ± 7.9	6 ± 1.3	3.8 ± 0.02
Melting point (°C)	171.4	168.2	160	172
% Degree Crystallinity	42.0	35.8	37.2	33.2

* Only one reading could be obtained

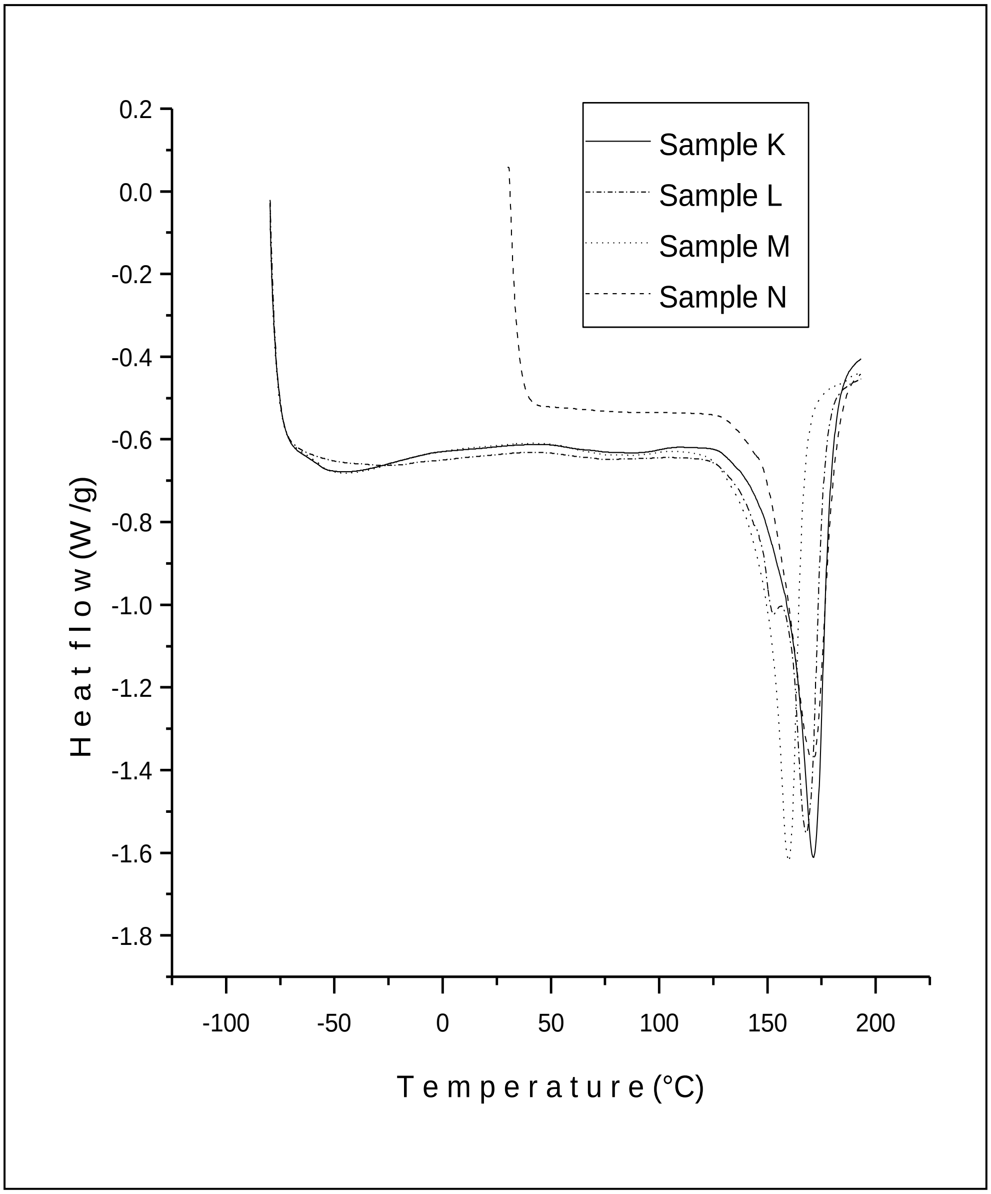


Figure 5.17 DSC plots for sample K, L, M, N

DMTA Analysis

Samples A, B, C, D (DRT: PP= 80: 20 approximately): DMTA plots for samples A, B, C and D were recorded (Figure 5.18). As expected, two Tgs (glass-transition temperatures) were clearly seen corresponding to SBR and PP at -50°C and 0°C respectively, in sample A (uncured blend). This suggests that the blends are not compatible and individual blend components hold on to their original Tgs. Sample B showed an increase in Tg (-30°C) for the rubber phase. As it was observed so far that sulphur did not significantly compatibilize the phases in sample B, the probable reason for this shift may be attributed to the curing of the rubber phase by sulphur. Curing is known to form crosslinks and hence, reduce the mobility of the molecules leading to an increase in Tg. The tan delta curve broadened, which suggests some extent of non-uniform interaction (such as non-uniform crosslinking) may have occurred between the rubber and PP phases. Sample C, which displayed better properties, showed a single and relatively sharper Tg peak at -45° C. A sharp Tg is interpreted as a good uniformity in the sample and hence, it can be said that sample C is uniformly compatibilized. This may be interpreted as the case of highest compatibilization among the four samples. Sample D shows a broader tan delta peak than sample C, indicating a non-uniform compatibilization.

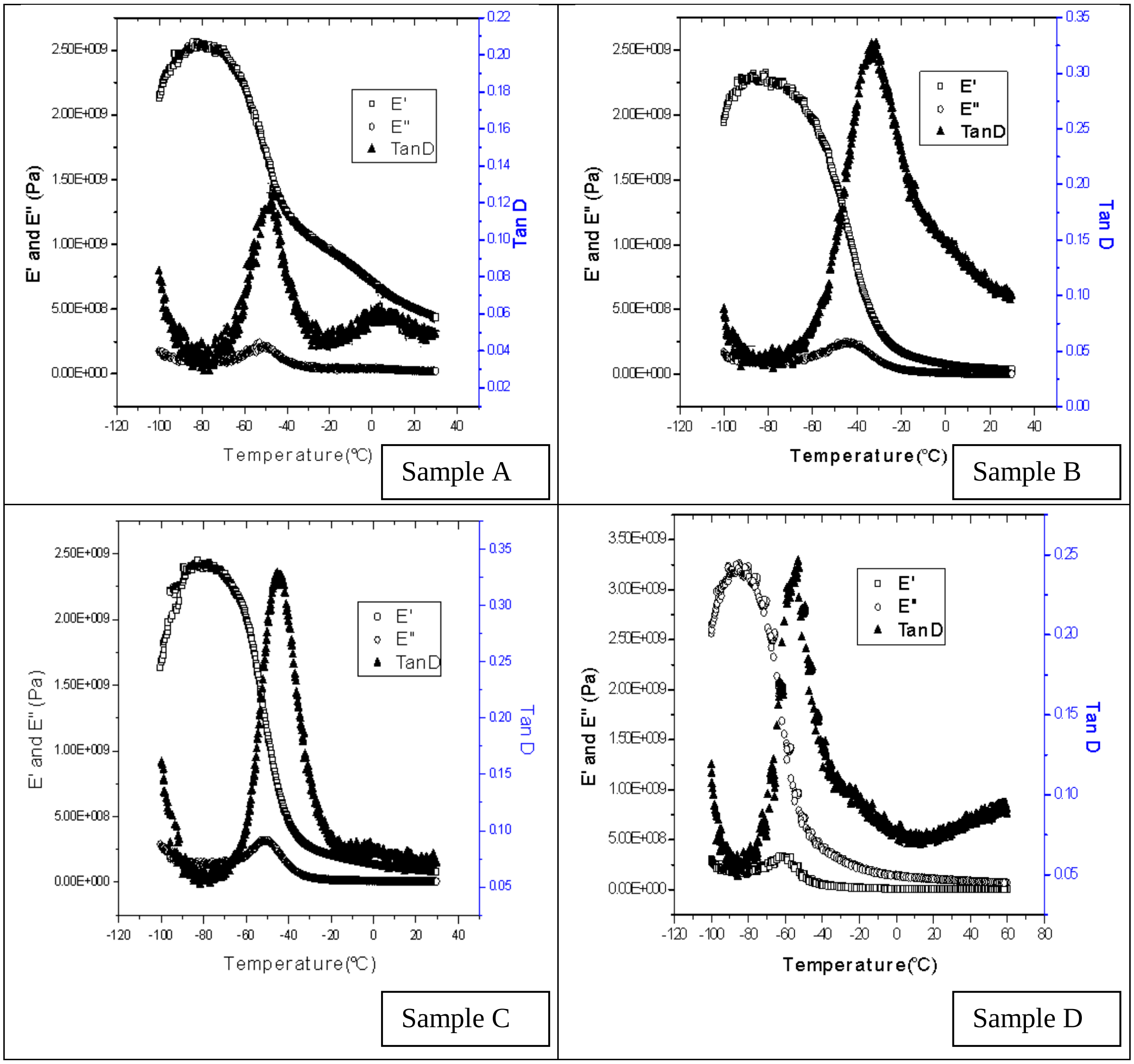


Figure 5.18 DMTA plots for samples A, B, C, D

It is found that the dynamic modulus (E’) of the blends depends on the crosslinking density (including interfacial reactions) and degree of crystallinity degree. On the one hand, an increase in crosslinking density favors an increase in E’. On the other hand, the higher degree of crosslinking prevents the alignment of the chains in the crystal lattice, hindering crystallization and leading to the decrease of the degree of crystallinity of PP, which favors a decrease in E’. Thus, a combined effect of the above mentioned factors influences E’ [12]. In case of samples B and C, the E’ values at -90°C are quite similar to the uncured sample A, as the above factors almost balance out each other. However, in sample D, there was a relatively smaller reduction in degree of crystallinity when compared to the increase in crosslink density (confirmed by sol content analysis (section 5.3.4)). Hence, it seems that the crosslink density is the predominant factor and an increase in E’ values was noted.

<u>Samples K, L, M, N</u> (DRT: PP= 40: 60 approximately): Sample K (uncured blend of DRT: PP= 40: 60) showed two Tgs (Figure 5.19) as expected. The one occurring at -60°C is for DRT, whereas, the one occurring around 0°C is typical for PP. Sample L, which was prepared with both sulphur and DCP and displayed better properties, shows the two Tgs getting closer to each other. This substantiates the claim that the DCP/ S system is superior in compatibilizing the DRT/ PP blends at low rubber content. Sample M had sulphur added to the system and it can be noticed that the tan delta curve was very broad, indicating rubber curing and a certain degree of non-homogenous compatibilization. In case of sample N (only DCP added), two distinct Tgs are seen. This suggests that DCP alone cannot compatibilize the phases, unlike the compositions having high DRT content. The E’ value of sample L is a little higher than the uncured blend, probably due to a greater increase in crosslink density (confirmed by sol content analysis) than reduction in degree of crystallinity. Sample M showed a value of E’ similar to that showed by the uncured sample. However, sample N recorded a decrease in crosslink density and degree of crystallinity as well. As both these factors did not cancel each other out, a reduction in E’ value is recorded.

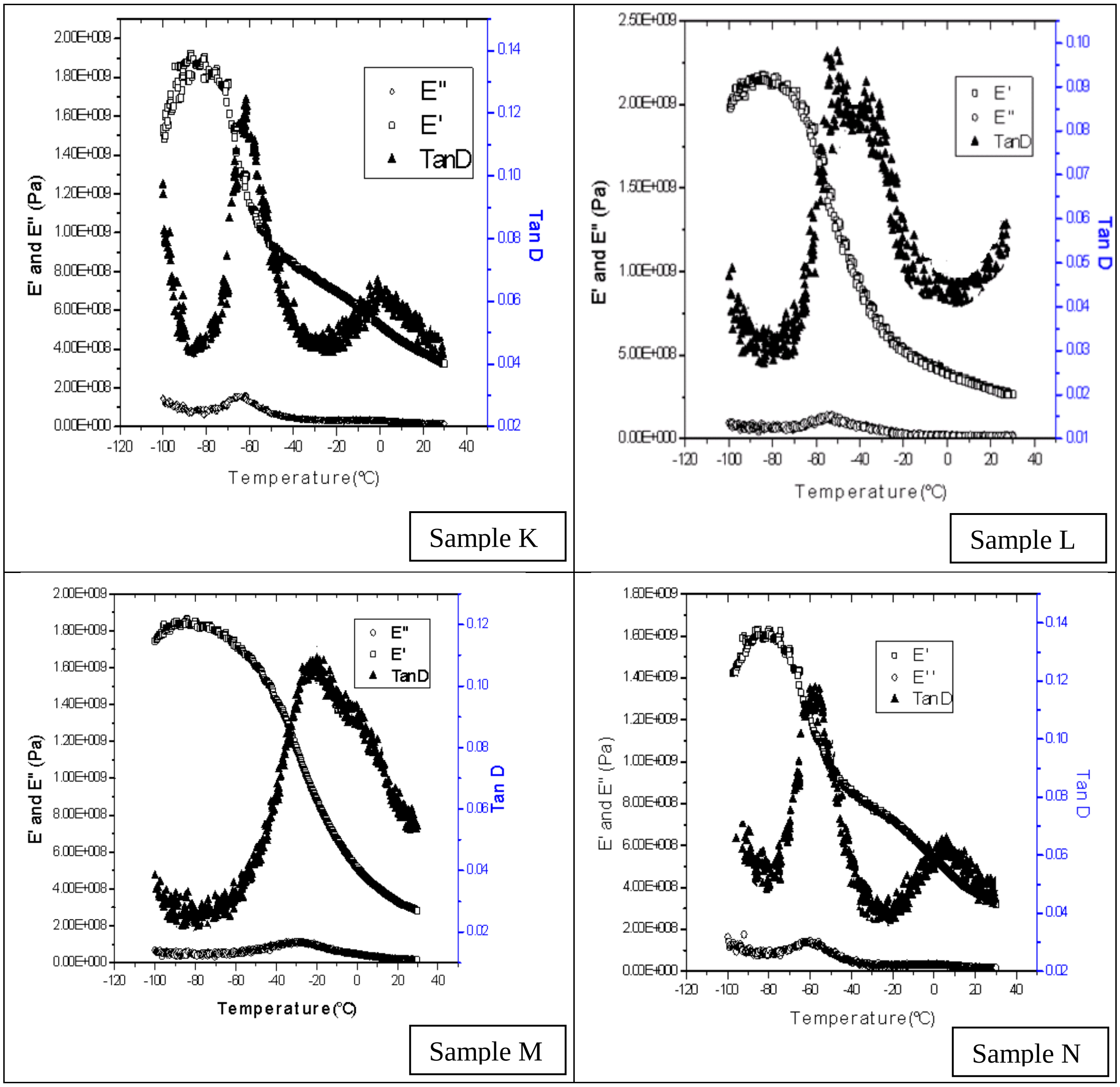


Figure 5.19 DMTA plots for samples K, L, M, N

5.3.4 Soluble Content

Samples A, B, C, D (DRT: PP= 80: 20 approximately): Soluble (sol) content for the samples was estimated by conducting a series of extractions (Table 5.7). Standard deviations of the centre point replicates came out to be 0.1, 0.1, 0.2 and 0.27 for %acetone extractable, %toluene extractable, %xylene extractable and %sol respectively. Thus, the reproducibility of the experiments looks very reasonable.

Table 5.7 Soluble content of blends with high rubber content

	Sample A (Uncured)	**Sample B (Only sulphur)**	**Sample C (Only DCP)**	**Sample D (Sulphur + DCP)**	**DRT**	**PP**
% Acetone extractable (AE)	5.23	4.97	3.67	2.97	5.53	0.0
% Toluene extractable (TE)	4.52	2.11	8.12	2.56	8.33	1.58
% Xylene extractable (XE)	12.17	11.75	1.99	5.37	2.02	44.35
% Sol (TE+XE)	16.52	13.86	10.11	7.93	15.87	45.93
TS (MPa)	2.5 ± 1.3	2.9 ± 0.08	8.4 ± 0.9	6.9 ± 0.5	--	--
EB (%)	30 ± 2	47 ± 13	72 ± 11	35 ± 7	--	--

As some of the rubber molecules can be extracted by xylene and some of the PP molecules can be extracted by toluene, one should be careful in evaluation each of the extraction values individually. In case of samples with high rubber content, it was noticed that sample D, cured with the DCP/S system, recorded the least sol content, although, sample C gave better properties. Thus, the gel content cannot be treated as a sole determining factor to estimate the properties of a material. This is because high gel content can result from crosslinks occurring within a phase; however, in order to get good properties, crosslinks have to occur between the phases as well. In sample D, sulphur might have caused crosslinks in the rubber phase resulting in an increase in gel content. But, in general, both C and D were found to be better compatibilized, and they showed a lower soluble content, when compared to samples A and B. In particular, sample C, showed a relatively higher toluene extractable and a far lesser xylene extractable. It is likely that some of the PP molecules were degraded and were extracted with toluene. Extraction results of fresh PP confirm that certain small molecular weight PP molecules are extractable by toluene.

Samples K, L, M, N (DRT: PP= 40: 60): It is noted that sample L, which displayed better properties, recorded the lowest sol content (Table 5.8). High gel content implies a higher crosslink density, and an improvement in properties indicates crosslinks occurred between the phases as well. This may be the reason for the improved performance of sample L. It should also be noted that the reduction in sol content majorly comes from a marked decrease in the percentage xylene extractable as was the case with sample C. This indicates that the DCP/S combination leads to crosslinking in the PP phase as well.

Table 5.8 Soluble content of blends with high plastic content

	Sample K (Uncured)	**Sample L (DCP+S)**	**Sample M (Only Sulphur)**	**Sample N (Only DCP)**
% Acetone extractable (AE)	3.69	3.80	0.74	0.47
% Toluene extractable (TE)	1.02	1.62	1.70	1.56
% Xylene extractable (XE)	15.32	7.76	21.41	20.33
% Sol (TE+ XE)	16.34	9.37	23.11	21.89
TS (MPa)	11.2 ± *	21.6 ± 1.2	10.3 ± 1.0	5.5 ± 0.24
EB (%)	8 ± *	20 ± 8	6 ± 1.3	4 ± 0.02

* Only one reading could be obtained

5.4 Conclusions

A detailed account of various reactions that sulphur and DCP may undergo in DRT/ PP blends is put forward in the introduction section of this chapter. The results obtained from various studies point to the hypothesis that when sulphur acts as a radical scavenger for DCP radicals (in the presence of low amount of plastic) and competes for double bonds, it causes a failure in the formation of a good interphase. On the other hand, when sulphur acts as a stabilizer for tertiary PP molecules (in the presence of abundant amount of plastic), it helps in the formation of a good interphase, leading to a positive interaction between DCP and sulphur. It is thought that sulphur has more affinity to react with tertiary PP radicals than with peroxide radicals or rubber unsaturation. Therefore, a higher plastic to rubber ratio (generating many tertiary PP radicals) would favor the use of a DCP and sulphur combination to get better properties; whereas, a higher rubber to plastic ratio would require the use of only DCP to get good properties. In other words, when the DRT content is much higher than PP, DCP alone is more effective in compatibilizing the phases and addition of sulphur retards the crosslinking efficiency. However, when the PP content is higher, use of a coagent (sulphur here) becomes mandatory to get good mechanical properties and morphology. Sulphur proved to be a good coagent to effectively reduce the beta-scission of PP and form sulphur bridges (when the PP content is high). The proposed hypothesis is consistent with the findings observed from various tests conducted on the samples. Hence, the mechanism of DCP/ S system is better understood as a result of this work. It would be interesting to see if the DCP/ S cure system follows the hypothesis in blends prepared from PP and DR produced from waste EPDM.

CHAPTER 6

DEVULCANIZED EPDM AND POLYPROPYLENE BLENDS

6.1 Introduction

In the previous chapter, a DCP based curing system was found effective in improving the properties of DRT/ PP blends. This chapter describes the results obtained by using this curing system on devulcanized EPDM/ PP based blends. The reason for choosing devulcanized EPDM (DRE) is that, EPDM is extensively used in automotive components. Therefore, it makes sense to explore the use of DRE in addition to DRT. Moreover, owing to the structural similarity between EPDM and PP, it may be possible to get blends with better properties than that obtained from DRT based on TPOs/ TPVs. Also, successful commercial TPVs (e.g. Santoprene) are based on EPDM/ PP blends. Additionally, this study would help to verify the hypothesis proposed regarding the mechanism of DCP/sulphur curing.

The efficiency of DCP curing depends on the concentration of readily abstractable hydrogens (due to unsaturation and chain branching) and the probability of chain scission. In general, the relative efficiency of peroxide vulcanization of rubbers is BR > NR & SBR > NBR > EPDM > EPR (ethylene-propylene rubbers) [1]. Peroxide crosslinking of highly unsaturated polymers is more efficient due to the higher concentration of allylic hydrogen, which are readily abstracted and efficiently converted to crosslinks. Loan [2] suggested that in case of EPR both the crosslinking and scission reactions (Figure 6.1) take place.

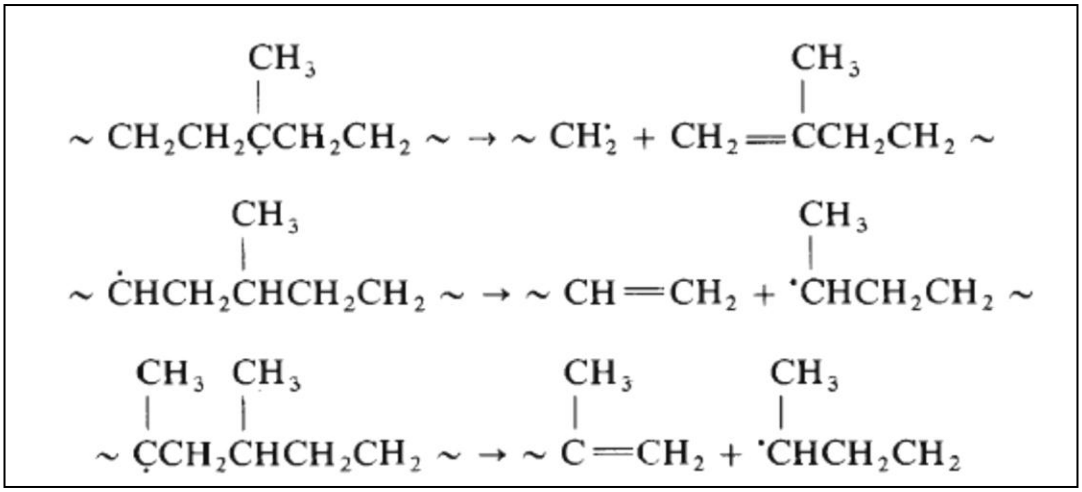
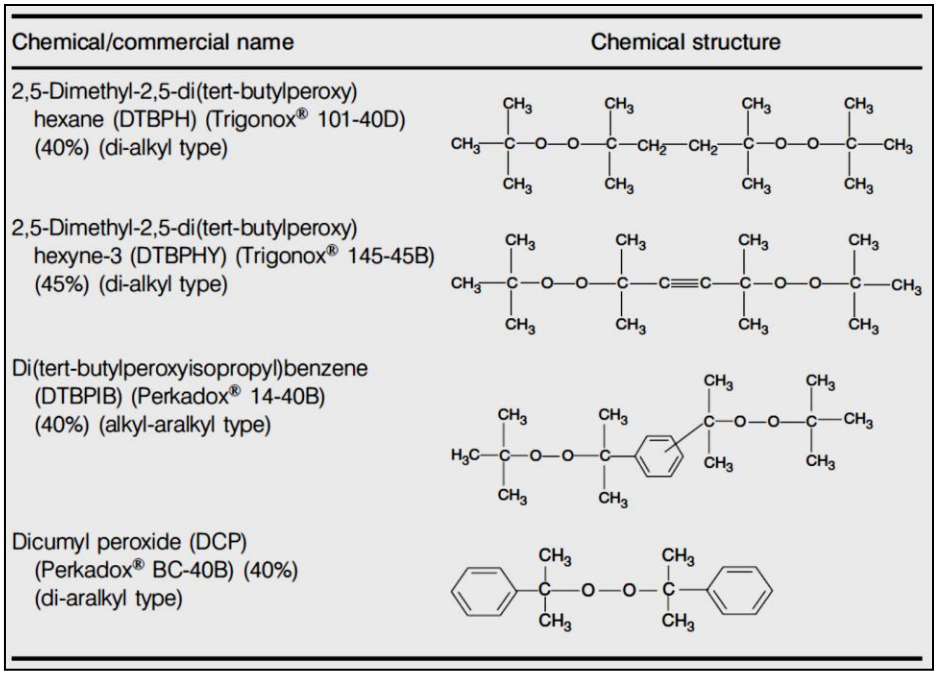


Figure 6.1 Possible scission reactions in ethylene-propylene rubbers [2]

The introduction of unsaturation into EPR has a marked effect on the crosslinking efficiency. The effects of scission are less pronounced in EPDM due to the presence of the unsaturated ter-monomer. The ter-monomer content of EPDM acts as the source of easily abstractable hydrogen atoms, which are useful in crosslinking [2, 3]. Whereas, the saturated copolymers show crosslinking efficiencies in the range 0.4 to 0.7, typical unsaturated ter-polymers may show efficiencies greater than unity [4, 5, 6 and 7].

Fujio et al. [8] found that introducing a small amount of sulphur (0.15 part by weight) into EPDM/ DVB (divinyl-benzene)/ DCP compounds, markedly increased Young’s modulus and the rupture energy of the vulcanizates. The swelling-equilibrium and dynamic mechanical behavior indicated an increase in the crosslink density. Naskar [9] investigated the effects of different types of peroxides as crosslinking agents at various PP/ EPDM blend ratios in dynamically vulcanized products. The TPVs were prepared by batch melt mixing of PP with EPDM, using various peroxides and triallyl-cyanurate (TAC) as coagent. Figure 6.2 lists the peroxides used in their work. The physical properties of the TPVs were found to change significantly with the PP/ EPDM blend ratios, chemical nature of the peroxides, the extent of crosslinking in the EPDM phase, and the extent of degradation in the PP phase. Irrespective of the PP/ EPDM blend ratios, in most cases, DCP out of four different types of peroxides investigated gave the best overall balance of physical properties.



Chemical/commercial name	Chemical structure
2,5-Dimethyl-2,5-di(tert-butylperoxy) hexane (DTBPH) (Trigonox® 101-40D) (40%) (di-alkyl type)	
2,5-Dimethyl-2,5-di(tert-butylperoxy) hexyne-3 (DTBPHY) (Trigonox® 145-45B) (45%) (di-alkyl type)	
Di(tert-butylperoxyisopropyl)benzene (DTBPIB) (Perkadox® 14-40B) (40%) (alkyl-aralkyl type)	
Dicumyl peroxide (DCP) (Perkadox® BC-40B) (40%) (di-aralkyl type)	

Figure 6.2 Various peroxides tested by Naskar [9]

Briefly recalling the mechanism proposed in the previous chapter, sulphur could be involved mainly in three types of reactions in our system. Firstly, sulphur can form crosslinks between rubber-rubber chains using the unsaturation sites. Secondly, it may react with DCP radicals and thus, act as radical scavenger. This would reduce the compatibilizing efficiency of DCP. Thirdly, it can react with tertiary radicals on PP molecules and stabilize them. Hence, by reducing beta-scission, and forming sulphur crosslinks a better compatibility may be achieved. This chapter describes the study carried out on devulcanized EPDM (DRE)/ PP blends and a comparison was made with DRT/ PP blends, wherever necessary. The goals of the work were to compare DRT and DRE based TPVs, and to evaluate the performance of DCP/ sulphur curing system on DRE based blends.

6.2 Experimental

6.2.1 Materials

The PP (PP31KK01, MFR = 5 g/10 mins) used had a TS of 24 MPa and 7% EB. DRE used had a TS of 10 MPa and an EB of 147%, when cured with standard sulphur based package (S=1.5, TBBS=1.5, ZnO=3, St. A=2 phr respectively). The curing system investigated for dynamic vulcanization consisted of DCP and/ or sulphur. Osmium-tetraoxide was used for staining purpose.

6.2.2 Experimental Design

A mixture design of experiments was adapted to analyze the effect of dosages of DRE, PP, DCP and sulphur on the mechanical properties. The range chosen for DCP and sulphur was 0% - 2%, whereas, for PP it was 20%- 60%, and for DR it was 40%- 80%. The dependent variables analyzed were tensile strength (TS) and elongation at break (EB). Three center-point replications were carried out to calculate pure error and LOF. Mixing was carried out in a Haake batch mixer as per the conditions mentioned in Chapter 3.

6.3 Results and Discussion

6.3.1 Mechanical properties

Table 6.1 and Table 6.2 summarize the results obtained. Results for sample N could not be obtained as it was significantly degraded and could not be molded in to a sheet. A look at the results indicate that when the DRE content was high (80%), use of DCP and sulphur together resulted in a material with better properties (an increase of 71% in TS, 75% in EB and 319% in breaking energy (BE) compared to uncured blend). On the other hand, at a low rubber content (40%), addition of curatives did not show any improvement. This was not the case for the devulcanized tire rubber (DRT), where it was observed that when the rubber content was high (80%), the presence of DCP as a curing agent produced a better material and at lower rubber content (40%), a combination of DCP and sulphur produced better results. The probable reasons for these results are discussed later in this chapter. On the whole, DRE seemed less effective than DRT in achieving better blend properties.

Analysis of the results using Statistica software reveals the variables, which significantly influenced the dependent factors (TS and EB). Linear models could not be fitted to the data as the LOF term was found to be significant. A cubic model was successfully fitted on the data for TS (Table 6.3) and a quadratic model for EB (Table 6.4).

Table 6.1 Experimental design and properties obtained

	A*	**B***	**C***	**D***	**K***	**L***	**M***	**N***
DRE (%)	80	78	78	76	40	40	40	40
PP (%)	20	20.0	20	20	60	56	58	58
PX (%)	0	0.0	2	2	0	2	0	2
S (%)	0	2	0	2	0	2	2	0
TS (MPa)	3.5 ±0.4	4.8 ±0.2	3.9 ±0.2	6 ±0.1	12 ±1	14.6 ±1	14.7 ±1.1	-
EB (%)	24 ±3.5	25 ±3.3	23 ±2.8	42 ±2	7 ±1	11 ±2	10 ±1.5	-
BE (J)	0.2 ±0.1	0.41 ±0.1	0.27 ±0.1	0.88 ±0.1	0.2 ±0.1	0.5 ±0.2	0.43 ±0.2	-

(- = No results could be obtained)

Table 6.2 Properties obtained at the center-point replications

	1	2	3
DRT	59.0	59.0	59.0
PP	39.0	39.0	39.0
DCP	1.0	1.0	1.0
S	1.0	1.0	1.0
TS (MPa)	8.2 ±0.3	7.4 ±1.0	11.5 ±0.2
EB (%)	13.3 ±1.1	10.8 ±3.0	12.8 ±1.2
BE (J)	0.3 ±0.1	0.2±0.2	0.5 ±0.1

Table 6.3 Overall Fit of the cubic model for TS

	SS	df	MS	F	p
Model	228.0426	6	38.00710	16.97240	0.008145
Total Error	8.9574	4	2.23935		
Lack of Fit	0.9574	2	0.47870	0.11967	0.893117
Pure Error	8.0000	2	4.00000		
Adjusted	237.0000	10	23.70000		

Table 6.4 Overall Fit of the quadratic model for EB

	SS	df	MS	F	p
Model	1381.091	7	197.2987	31.03928	0.008459
Total Error	19.069	3	6.3564		
Lack of Fit	15.689	1	15.6893	9.28359	0.092944
Pure Error	3.380	2	1.6900		
Adjusted	1400.160	10	140.0160		

As seen from the Pareto chart (Figure 6.3), TS is significantly influenced by the interaction between ‘PP, DCP and sulphur’ (PP-DCP-S). This may be interpreted as a reflection of the stabilizing role of sulphur by reacting with tertiary PP radicals in order to prevent beta scission. On the other hand, EB (Figure 6.4) is significantly influenced (negatively) by the interactions between ‘PP-DCP’, ‘DRE-DCP’ and ‘PP-DRE’. These may be indications of the degrading effect of DCP on DRE and PP, and incompatibility between the two phases. The models were validated using a plot of predicted versus observed values (Figure 6.5 and Figure 6.6).

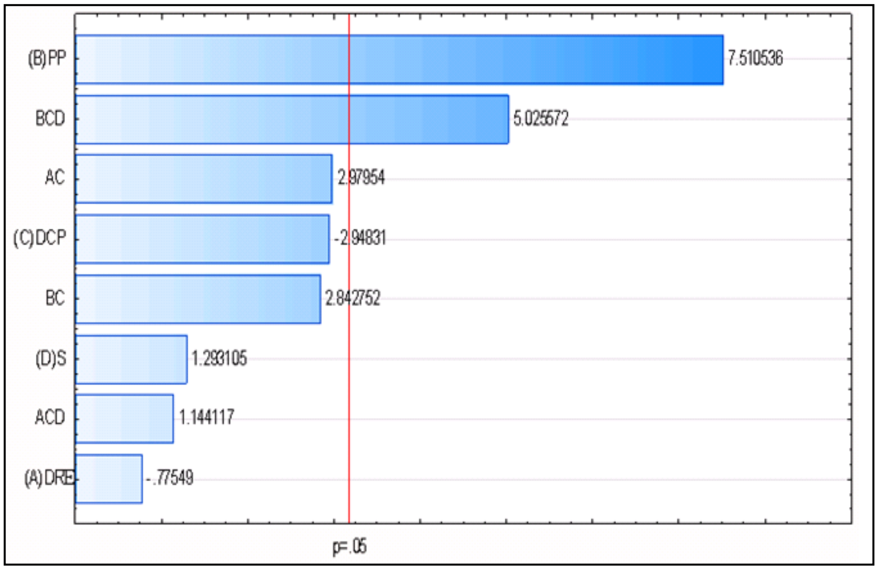


Figure 6.3 Pareto chart for TS

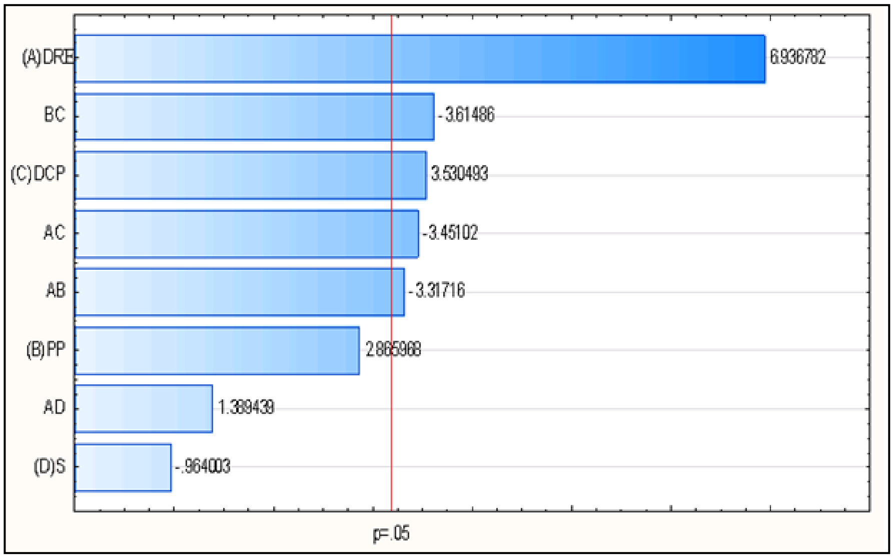


Figure 6.4 Pareto chart for EB

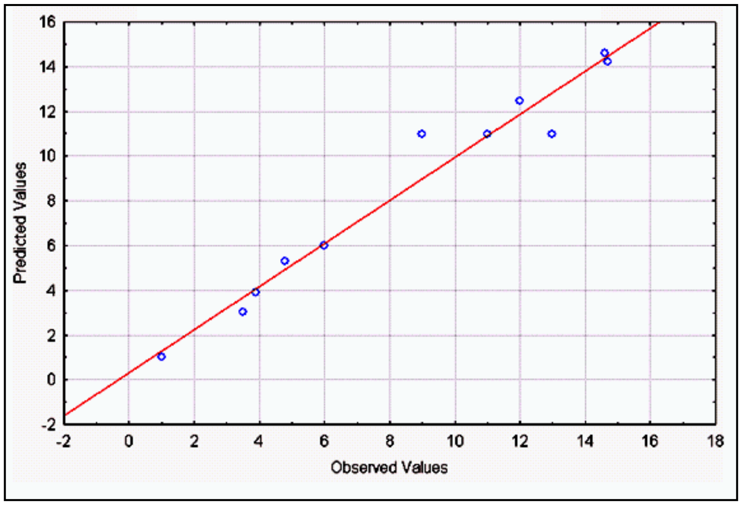


Figure 6.5 Predicted versus observed values (TS)

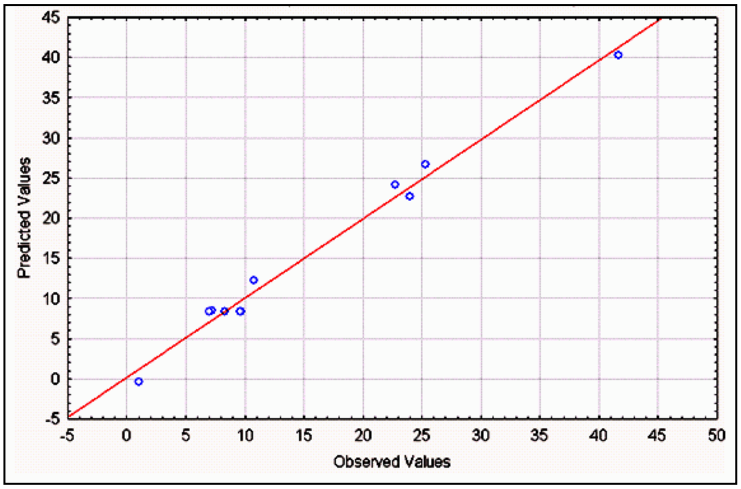


Figure 6.6 Predicted versus observed values (EB)

The coefficients of the various interactions were used to form model equations (Equations 6.1 and 6.2), which can predict the dependent variable for any given composition, as long as the values for the independent variables lie within the range chosen for the experiments. The significant variables and their coefficients are highlighted in the model equations.

$\mathbf{TS} = -\mathbf{0.017}(\mathbf{DRE}) + \mathbf{0.219}(\mathbf{PP}) - \mathbf{329.606}(\mathbf{DCP}) + \mathbf{1.101}(\mathbf{S}) + \mathbf{3.399}(\mathbf{DRE} - \mathbf{DCP}) + \mathbf{3.244}(\mathbf{PP} - \mathbf{S}) + \mathbf{0.019}(\mathbf{DRE} - \mathbf{DCP} - \mathbf{S}) + \mathbf{0.097}(\mathbf{PP} - \mathbf{DCP} - \mathbf{S})$…………………………………..Equation 6.1

$$\mathbf{EB} = \mathbf{0.5DRE} + \mathbf{0.51PP} + \mathbf{305.49}(\mathbf{DCP}) - \mathbf{2.9195}(\mathbf{S}) - \mathbf{0.0177}(\mathbf{DRE} - \mathbf{PP}) - \mathbf{3.0783}(\mathbf{DRE} - \mathbf{DCP}) + \mathbf{0.00652}(\mathbf{DRE} - \mathbf{S}) - \mathbf{3.2244}(\mathbf{PP} - \mathbf{DCP})$$

………………………………………………………………………………...Equation 6.2

6.3.2 Morphology

Samples A*, B*, C*, D* (DRE: PP= 80: 20 approximately)

SEM pictures of the four samples were taken at 200X and 1kX magnifications (Figure 6.7 and Figure 6.8), although differences are easily noticeable in 200X images. A look at SEM pictures for sample A* indicates the presence of bright large rubber crumbs and voids. However, the matrix phase looks more uniform and compatibilized than in the case of DRT blends having similar composition. This may be due to the structural similarity between EPDM and PP. However, the presence of larger crumb rubber particles may have counter-weighed the advantage of a good mixing in the matrix resulting in mechanical properties similar to that shown by DRT.

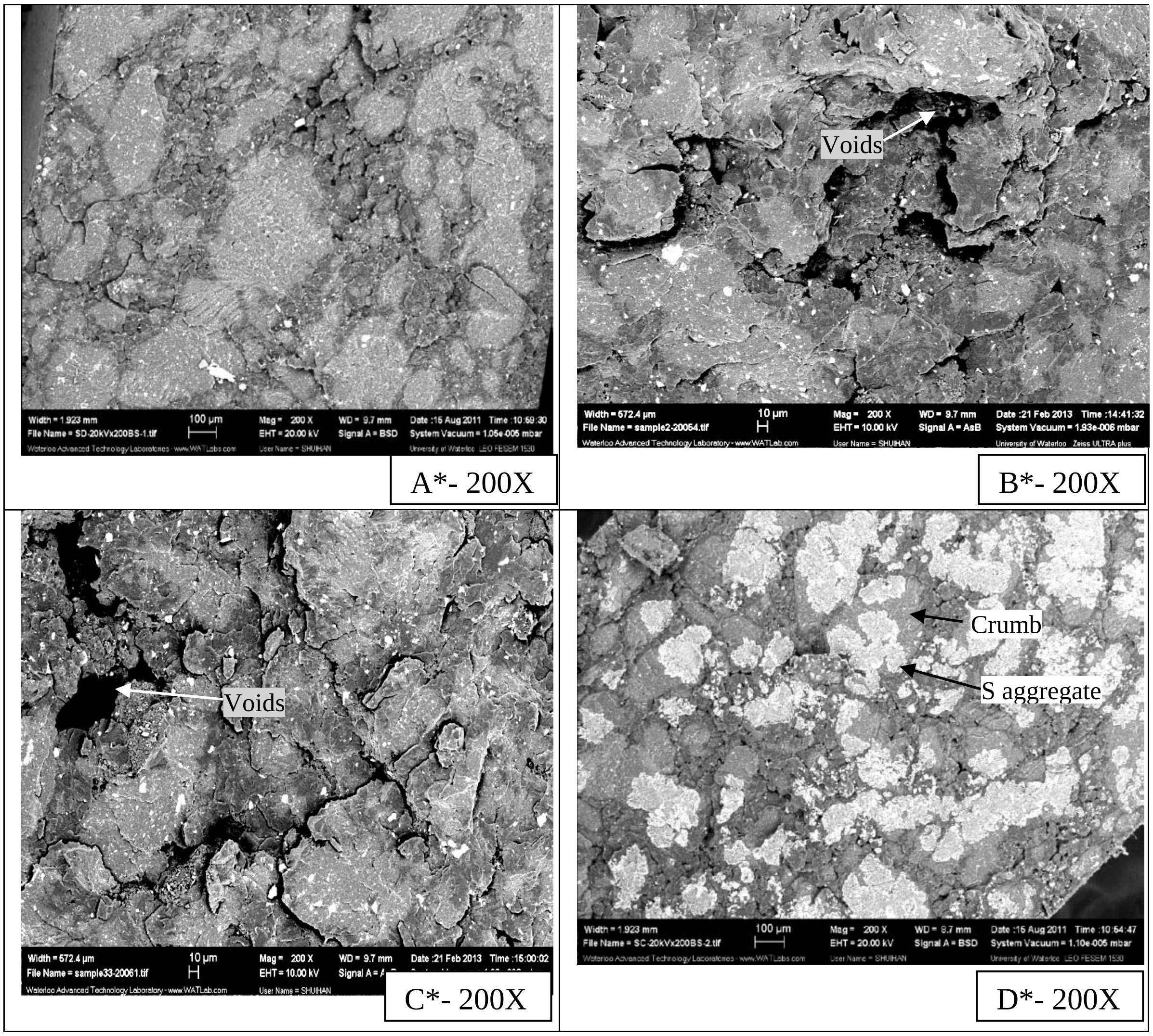


Figure 6.7 SEM images of the samples A*, B*, C*, D* at 200X

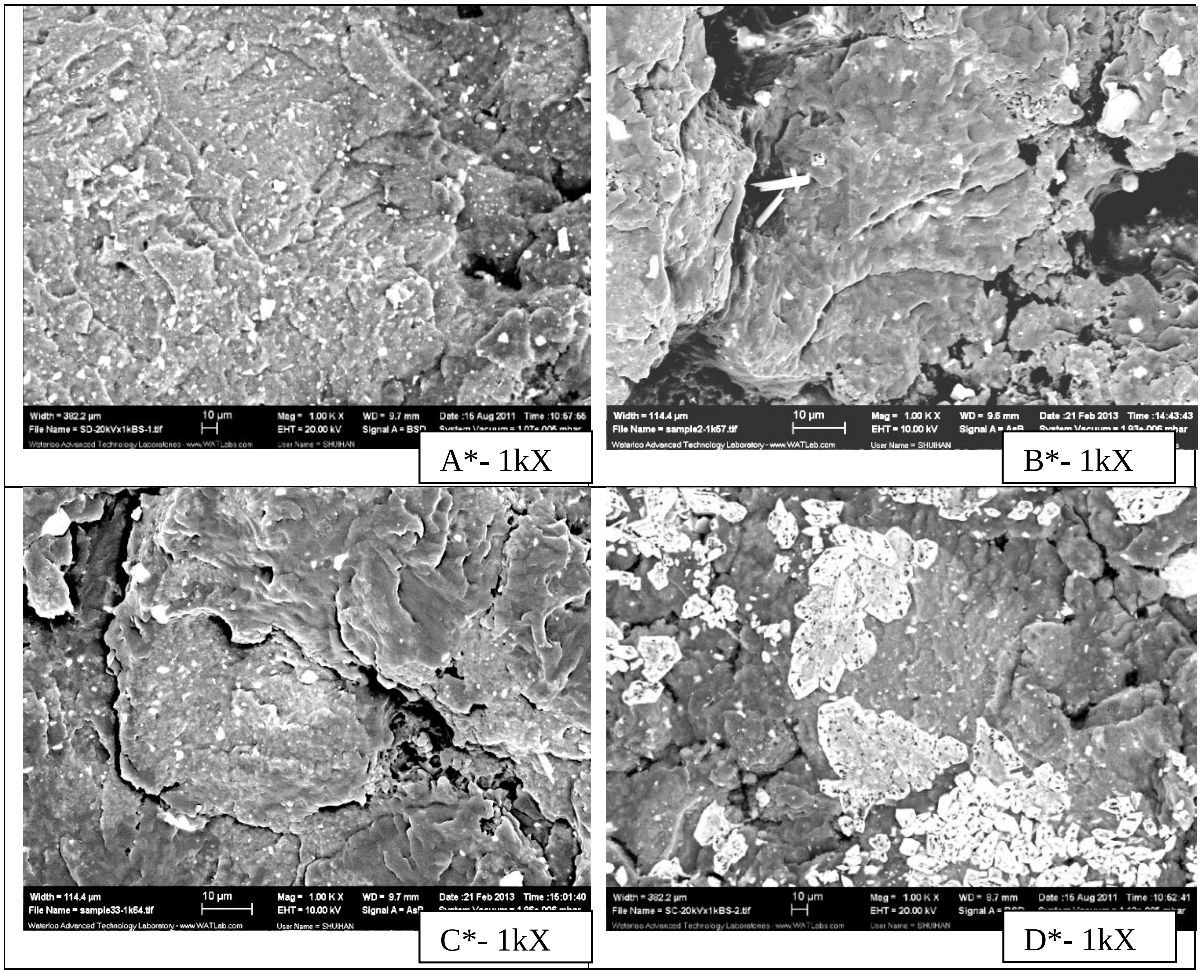


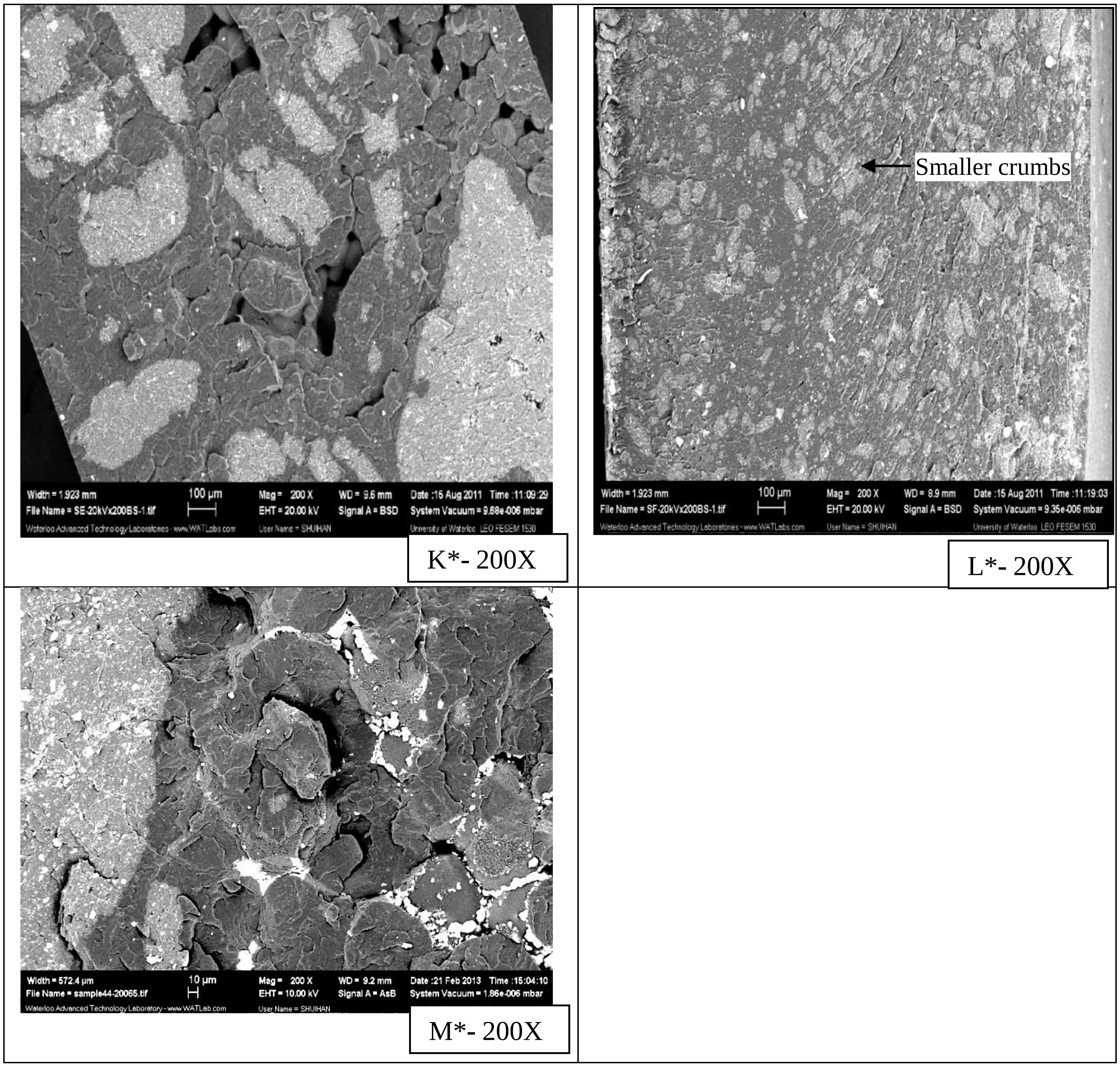
Figure 6.8 **SEM images of the samples A*, B*, C*, D* at 1kX**

Samples B* and C*, upon addition of sulphur and DCP respectively, showed an increase in voids, which may have resulted due to increased differential thermal shrinkage. It should be noted that sample C* showed no significant changes in the properties, whereas, there was a significant increase in properties in the case of DRT (sample C). As all other variables were the same, this implies that the rubber structures too play a crucial role. The probable reasons to explain this difference are discussed here. In the case of DRT, the rubber chains are not susceptible to degradation by DCP radicals. But, in the case of DRE, DCP has the potential to degrade the PP segments of the rubber chains, in addition to the plastic phase consisting of PP. Hence, there is an increase in the number of degradation reactions, which balanced out the crosslinking reactions. Generally EPR (ethylene propylene rubber) tends to be more prone to degradation, as in the case of EPDM, crosslinking reactions are significantly dominant due to the presence of unsaturation [11]. This hints to the possibility that, as the rubber is already vulcanized and then aged during the service period, and later on subjected to mechanical grinding process, the amount of unsaturation has reduced and it behaved similar to EPR.

In sample D*, sulphur addition along with DCP led to a material having better properties, which was not the case in DRT. The morphology of sample D* (Figure 6.7) shows less voids and some bright aggregations are observed on the rubber crumbs, which were confirmed by EDX (energy-dispersive X-ray spectroscopy) analysis to be consisting of sulphur. Thus, it seems that sulphur prevented the degradation of PP and DRE by preferably reacting with the tertiary radical sites on PP units to stabilize them, and formed interphase through C-S-C sulphur bridges. The highly crosslinked structure between the two phases leads to a stronger interphase, which resulted in the superior properties for this sample. In the case of DRT blends, sulphur acted as a DCP radical scavenger and competed for double bonds (reducing the crosslinking efficiency of DCP), but in the case of DRE blends, it acted as a stabilizer. This supports the hypothesis that sulphur has more affinity to react with tertiary radical sites than with DCP radicals or double bonds.

Samples K*, L*, M*, N* (DRE: PP= 40: 60 approximately)

SEM images at 200X and 1kX were taken only for samples K*, L* and M* (Figure 6.9 and Figure 6.10) as sample N* was markedly degraded and could not be molded into a plaque. Addition of curatives did not significantly improve the properties of any of these samples. As was the case with high rubber content compositions, uncured blends of DRE and DRT with PP showed similar properties. Sample M*, with addition of sulphur, did not show any major change in properties. The morphology was also similar to the uncured blend. In the case of sample L*, addition of sulphur along with DCP, showed a negligible increase in mechanical properties compared to the uncured blend. However, it should be noted that the material was not degraded. Sample L* looks more homogenous and shows less voids along with smaller crumbs, which may be contributing to its improved breaking energy (BE). In the case of DRT (sample L), a combination of sulphur and DCP gave better results than uncured blends in terms of mechanical properties due to the stabilizing action of sulphur. This once again suggests that the rubber structures play a crucial role. In the case of DRE, although sulphur prevented degradation of the PP links, it seems that the amount of sulphur was not sufficient to induce an improvement in properties considering that there was an abundance of beta-scission degradable sites (coming from both DRE and PP). A high PP dosage in these four samples further increased the concentration of those sites. Thus, degrading and stabilizing reactions may have been balanced out leading to no major change in the properties. Probably an increased level of sulphur dosage may show improvements in the properties.

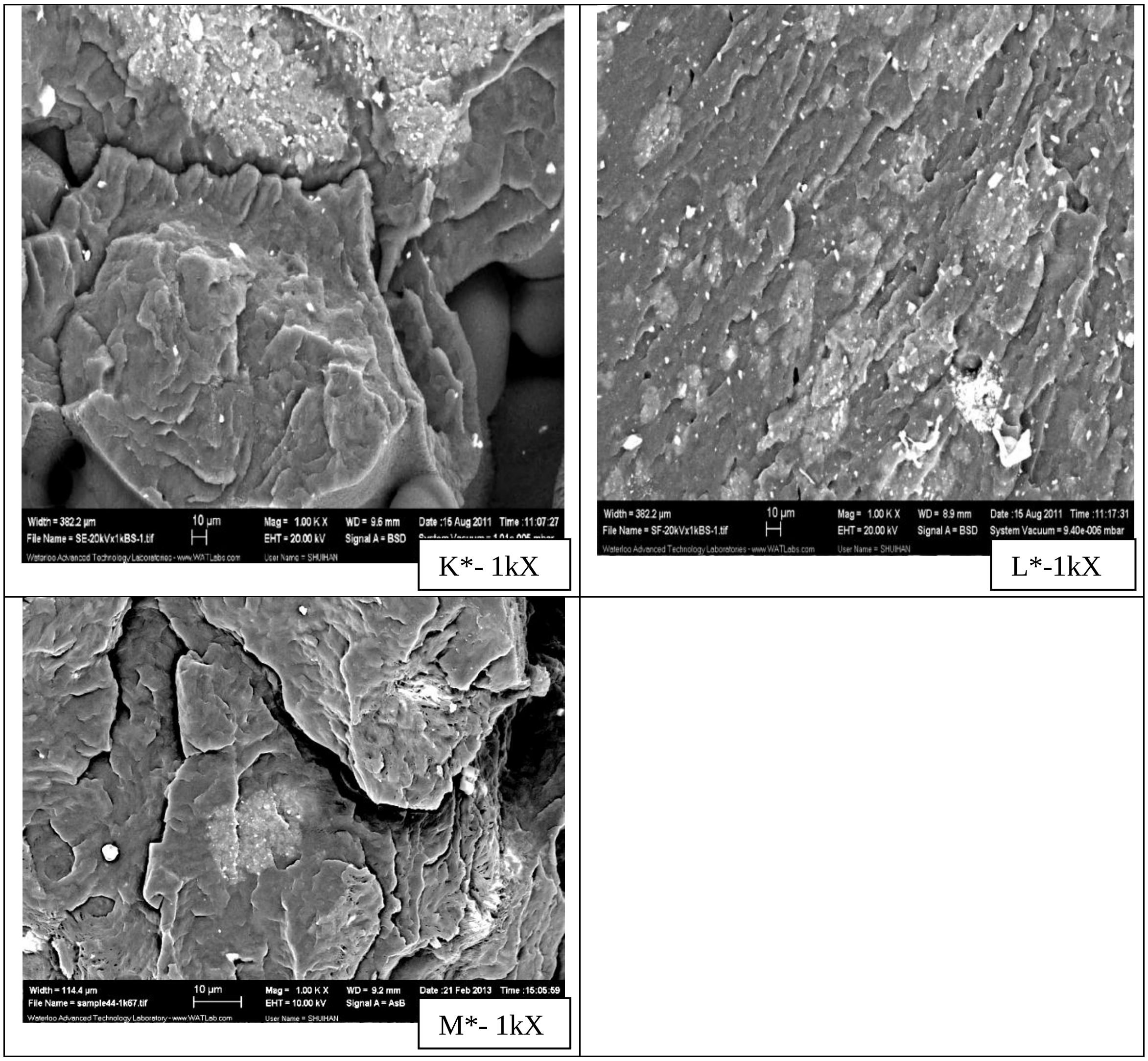


K*- 200X

L*- 200X

M*- 200X

Figure 6.9 SEM images of samples K*, L*, M* at 200X



K*- 1kX

L*-1kX

M*- 1kX

Figure 6.10 **SEM images of samples K*, L*, M* at 1kX**

6.3.3 Thermal Studies

DSC Tests

Samples A*, B*, C*, D* (DRE: PP= 80: 20 approximately): DSC tests were conducted to determine the percentage crystallinity and melting points of the blends (Table 6.5). Figure 6.11 shows the corresponding plots. Replications of the centre-point sample yielded a standard deviation of 3.5 units for degree of crystallinity values and 1.2 units for melting temperature. It can be seen that sample D*, which gave better properties, showed a 15% drop in degree of crystallinity, and a 4% reduction in melting temperature compared to the uncured blend. It is known that compatibilization leads to a reduction in the degree of crystallinity and melting temperature. Hence, this supports the assumption that sample D* is compatibilized by the DCP/S system. However, when DCP is used alone there is a further reduction in the degree of crystallinity and melting temperatures. As it is known from the mechanical properties that the phases are not compatibilized, this may be associated with the degradation caused by DCP. Degradation results in a lower molecular weight resulting from shorter chains, which makes it difficult for the chains to fold and align in order to crystallize.

Table 6.5 Melting point and degree of crystallinity for blends with high rubber content

	Sample A* (Uncured)	**Sample B* (Only sulphur)**	**Sample C* (Only DCP)**	**Sample D* (Sulphur + DCP)**
TS (MPa)	3.5 ± 0.4	4.8 ± 0.2	3.9 ± 0.2	6.0 ± 0.1
EB (%)	24 ± 3.5	25 ± 3.3	23 ± 2.8	42 ± 2
Melting point (°C)	161.7	159.6	149.6	156.1
% Degree of Crystallinity	45.70	45.0	34.6	38.8

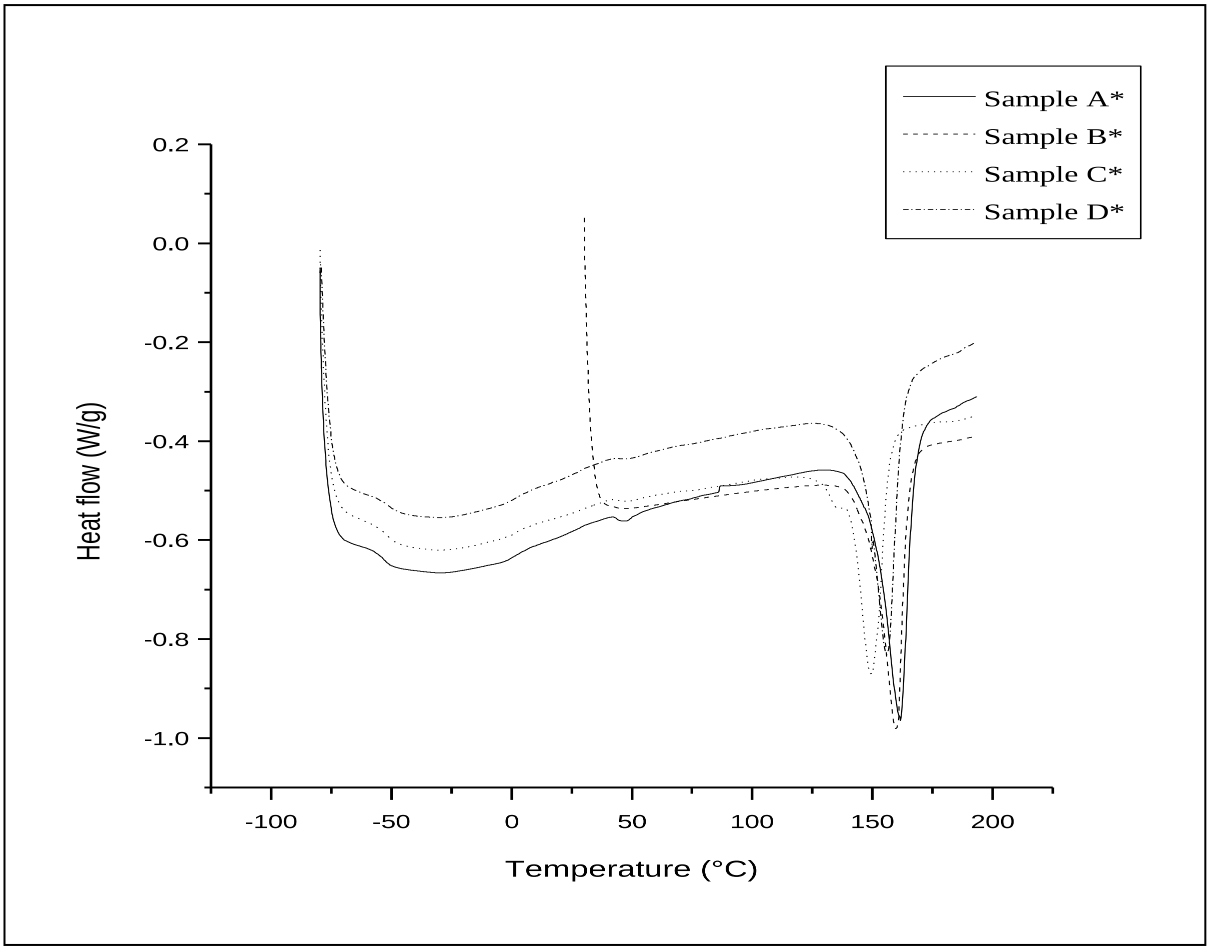


Figure 6.11 DSC plots for sample A*, B*, C*, D*

Samples K*, L*, M*, N* (DRE: PP= 40: 60 approximately): A reduction in melting point is seen for samples with curatives (Table 6.6). However, there is no significant drop in the degree of crystallinity in samples L* and M*. Hence, as suspected, sample L* is not well compatibilized, although it seems more compatibilized than sample M*. Sample N* (only DCP added), showed a significant drop in the degree of crystallinity and MP. As in the case with high rubber content, this may be associated with the degradation reactions that occurred. Corresponding DSC plots are shown in Figure 6.12.

Table 6.6 Melting point and degree of crystallinity for TPOs/ TPVs with low rubber content

	Sample K*(Uncured)	**Sample L* (DCP+S)**	**Sample M* (Only Sulphur)**	**Sample N* (Only DCP)**
TS (MPa)	12.0 ± 1	14.6 ± 1	14.7 ± 1.1	-
EB (%)	7 ± 1	11.0 ± 2	10.0 ± 1.5	-
Melting point (°C)	168.6	162.5	166.9	157.8
% Degree Crystallinity	39.2	38.0	39.5	26.9

- Readings could not be obtained

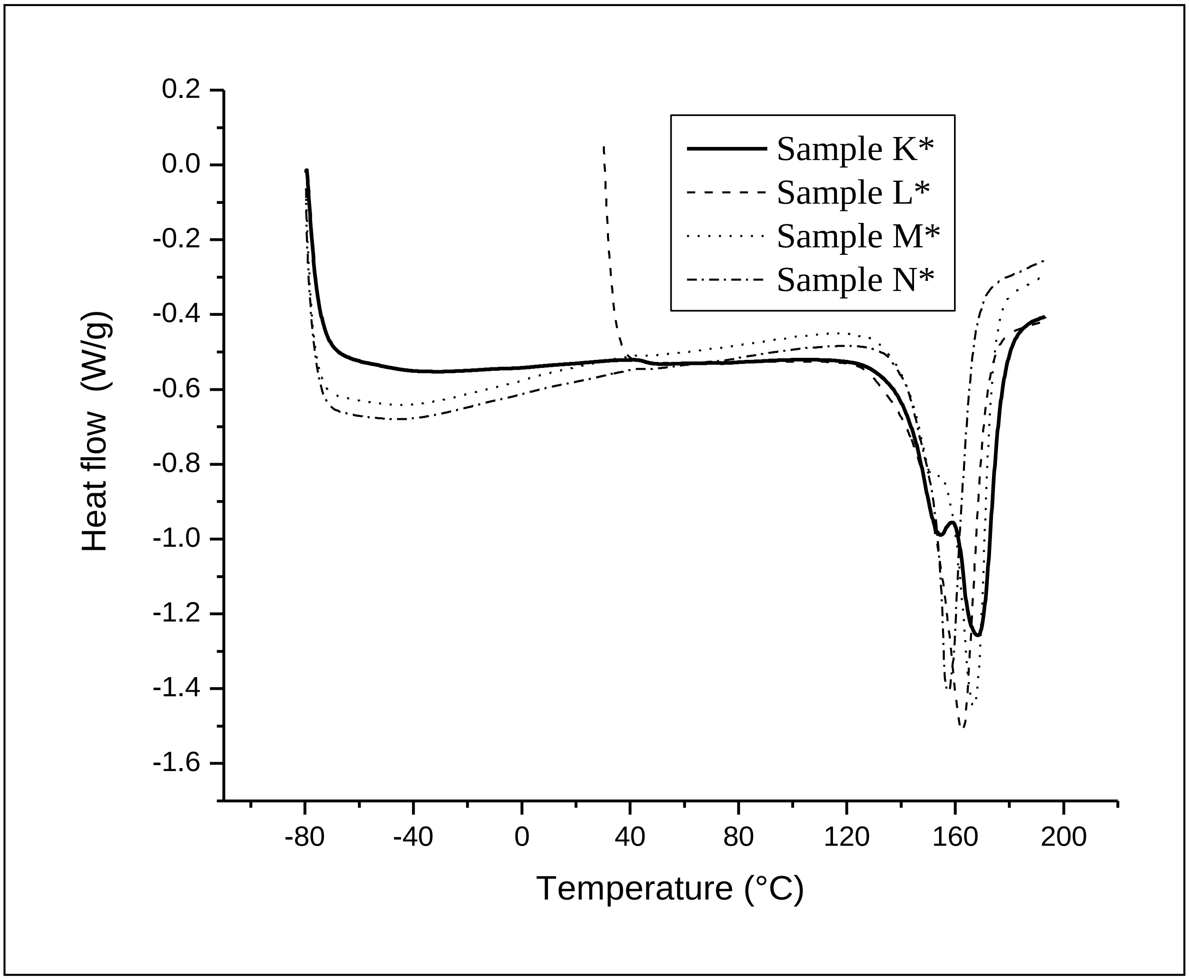
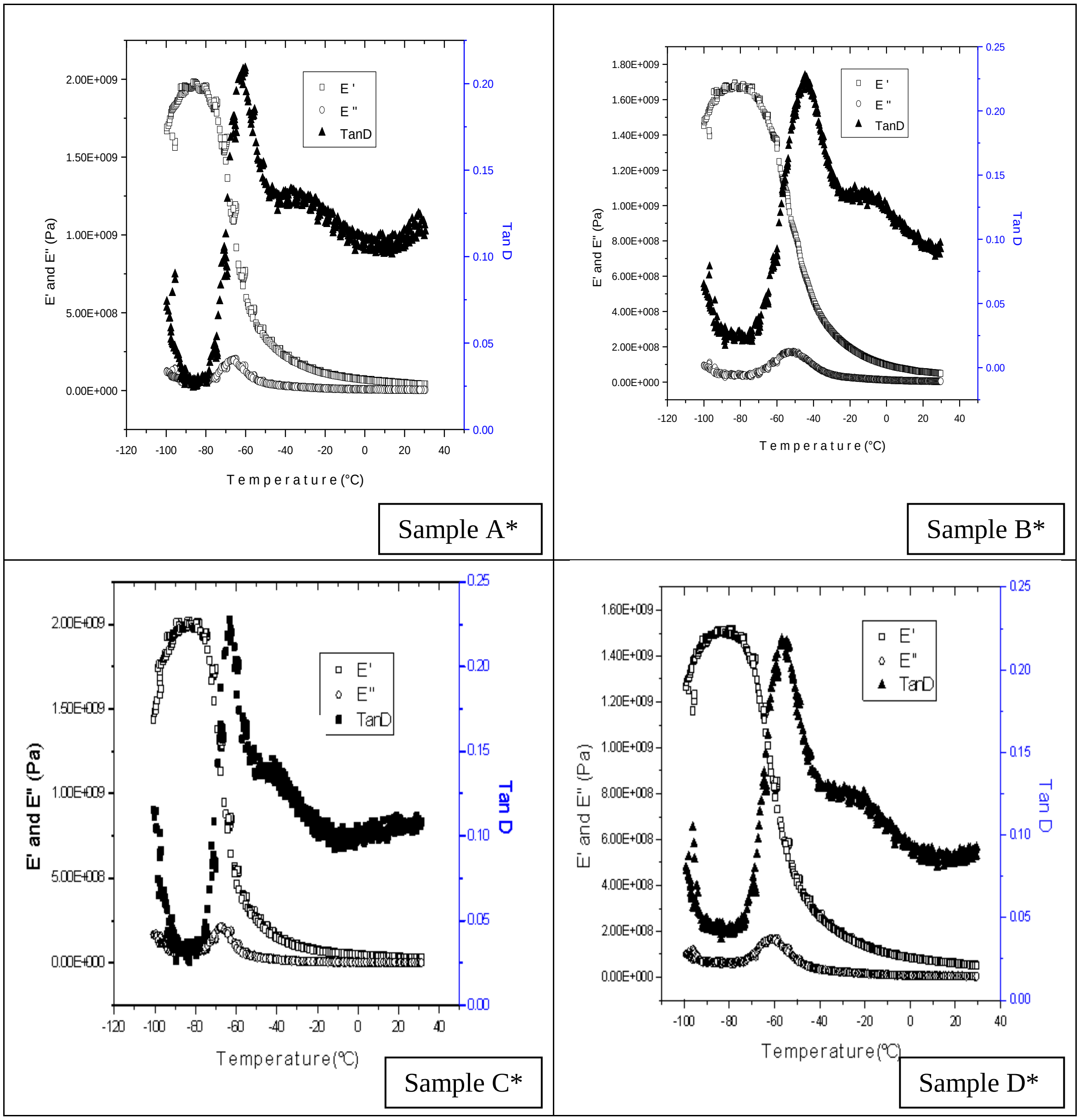


Figure 6.12 DSC plots for sample K*, L*, M*, N*

DMTA Analysis

Samples A*, B*, C*, D* (DRE: PP= 80: 20 approximately): Figure 6.13 shows the DMTA plots for all the four samples. Sample A* shows two distinct Tgs for EPDM (-60 °C approximately) and PP (-30°C) phases. However, the typical value for Tg of PP is 0°C. Thus, it indicates that the phases compatibilized to a certain extent, owing to the similarity in the chemical structures. In sample B*, with addition of sulfur, the Tg of PP increased to its typical value of 0°C, and the Tg of the rubber phase is found to increase too. This may be caused by crosslinking within the rubber phase, which is known to increase Tg. This may have resulted in an increase in incompatibility between the phases causing the Tg of PP to increase. In case of sample C*, Tg of rubber remains intact at -60°C, but Tg of PP is decreased to -40°C, which may be associated with the degradation of PP molecules. Degradation may shorten the chain lengths resulting in an increase mobility, which in turn leads to a reduction in Tg. The plot for sample D*, which gave better properties, displayed slightly better compatibility with both the peaks converging towards each other. The rubber Tg is displaced to about -50°C and Tg of PP reaches -25°C. Thus, addition of sulphur along with DCP seems to increase the compatibility of the two phases. The E' value of sampled D* is reduced when compared to the uncured blend. This may be attributed to the reduction in degree of crystallinity, which is known to reduce E'.



Sample A*

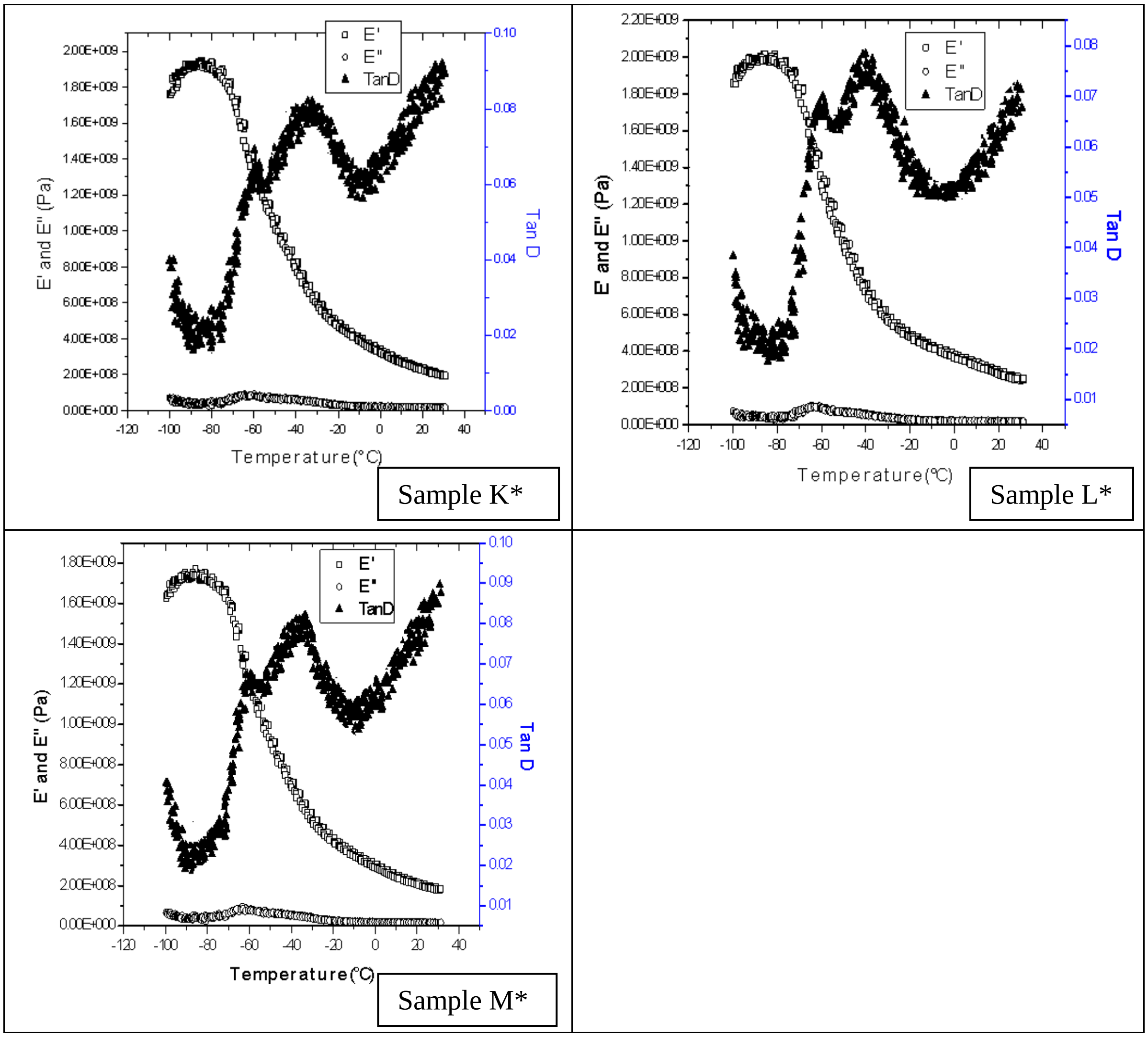
Sample B*

Sample C*

Sample D*

Figure 6.13 DMTA plots for samples A*, B*, C*, D*

<u>Samples K*, L*, M*, N*</u> (DRE: PP= 40: 60 approximately): In sample K* and M*, two distinct Tgs are visible at -60°C and -35°C corresponding to DRE and PP respectively (Figure 6.14). This suggests that addition of sulphur did not compatibilize the phases. In sample L*, there is a slight reduction of the Tg of PP to -40°C indicating a little improvement in compatibility. Sample N* was extensively degraded and hence, could not be tested.



Sample K*

Sample L*

Sample M*

Figure 6.14 DMTA plots of samples K*, L*, M*

6.3.4 Soluble Content

Percentage change in weight of the samples after being extracted by acetone, toluene and xylene one after the other were tabulated. Standard deviations of the centre point replicates were found to be 0.1, 0.1, 0.2 and 0.27 for %acetone extractables, %toluene extractables, %xylene extractables and %sol respectively. Thus, the reproducibility of the experiments looked reasonable.

<u>Samples A*, B*, C*, D*</u> (DRE: PP= 80: 20): In case of samples with high rubber content (Table 6.7), it was noticed that the sol content is the least for sample D* (cured with the DCP/S system), which displayed better properties. The main contribution towards this reduction came from the xylene extractable. DMTA analysis and SEM images confirmed that sample D* is most compatibilized, and hence, it seems that the crosslinks occurred between the phases as well. Thus, the mechanical properties of the samples were better. Sample B* and C* showed similar values as the uncured blend and accordingly there was no major improvement in their properties as well.

Table 6.7 Soluble content of blends with high rubber content

	Sample A* (Uncured)	**Sample B* (Only Sulphur)**	**Sample C* (Only DCP)**	**Sample D* (Sulphur + DCP)**	**DRE**	**PP**
% Acetone extractable (AE)	11.92	11.01	11.84	12.04	14.16	0.00
% Toluene extractable (TE)	1.65	3.33	0.86	1.64	2.82	1.58
% Xylene extractable (XE)	10.38	11.87	11.27	5.43	0.27	44.35
% Sol (XE+TE)	23.95	26.21	23.98	19.12	17.24	45.93
TS (MPa)	3.5 ± 0.4	3.9 ± 0.2	4.8 ± 0.2	6.0 ± 0.1	--	--
EB (%)	24 ± 3.5	22.75 ± 2.8	25.3 ± 3.3	41.7 ± 2.0	--	--

<u>Samples K*, L*, M* and N*</u> (DRE: PP= 40: 60): Sample L* (cured with DCP/S) showed the least sol content (Table 6.8), although all three samples K, L and M showed similar properties. The major contribution towards this reduction comes from the xylene extractable, which is supposed to be rich in uncrosslinked PP molecules. Thus, it seems that the gel

content cannot be treated as a sole indicator of good compatibility and properties. A high gel content can result from crosslinking within the phases, however to get good properties, crosslinks need to be formed between the phases as well. It is suspected that the crosslinks occurred majorly in the PP phase in sample L*.

Table 6.8 Soluble content of blends with low rubber content

	Sample K* (Uncured)	**Sample L* (Sulphur+ DCP)**	**Sample M* (Only sulphur)**	**Sample N* (Only DCP)**
% Acetone extractable (AE)	4.83	6.98	7.44	3.92
% Toluene extractable (TE)	1.68	1.12	0.78	1.1
% Xylene extractable (XE)	22.86	5.83	22.18	29.72
% Sol (XE+TE)	24.54	6.95	22.96	30.82
TS (MPa)	12 ± 1	14.6 ± 1.0	14.7 ± 1.1	--
EB (%)	7.2 ± 1	10.8 ± 2.0	9. 7 ± 1.5	--

-- Readings could not be obtained

Sample N*, which was expected to be degraded as it had only DCP added to it, showed the highest sol content whereas, sample L* (having sulphur with DCP) showed the least. This once again reinforces the stabilizing action of sulphur.

6.4 Conclusions

The results showed that for DCP to be an effective cure compatibilizer for DRE/ PP blends, the presence of sulphur is essential at all compositions (unlike in the case of blends of DRT: PP= 80: 20). This is because both EPDM and PP are susceptible to beta-scission by DCP radicals. Sulphur proved to be a good coagent to effectively reduce beta-scission of PP and EPDM by forming sulphur bridges, which resulted in an improved morphology. However, when the PP content was higher, it looked like sulphur may be required at higher amounts in order to improve the properties. An experimental design with different DCP: Sulphur ratios would help to confirm this hypothesis. The action of sulphur as DCP radical scavenger or competing for double bonds is not evident in DRE/ PP blends. Hence, as proposed in the previous chapter, sulphur seems to have more affinity to react with tertiary PP radicals than with peroxide radicals or double bonds. Therefore, in the case of DRE/ PP blends, irrespective of the ratio of rubber to PP, due to the abundance of tertiary radicals from both the phases, sulphur mainly acted as a stabilizer. Hence, the mechanism proposed in Chapter 5 regarding DCP/S system seems to hold well. On the whole, DRT seems a better choice than DRE based on the current knowledge of the blends.

The mixing carried out so far was in a batch mixer. It is believed that the properties may be further improved by preparing the blends in a TSE as the material would be exposed to higher shear forces resulting in smaller rubber domains. It would be interesting to see if this could lead to a significant improvement in the blend properties.

CHAPTER 7

DYNAMIC VULCANIZATION OF TPVs IN A TWIN SCREW EXTRUDER

7.1 Introduction

From the results discussed so far, it was found that non-reactive compatibilization was not very effective, whereas, reactive method based on DCP was to some extent successful in compatibilizing the blends. The reason for this finding was associated with the presence of crumb rubber, which seemed reluctant to react with the matrix and hence, continued to act as stress concentrators. DCP curing was found to initiate reactions of the double bonds in those crumbs with the matrix and thus, improve the interfacial adhesion and properties. However, addition of non-reactive compatibilizers with the curing agents was not tested. Also, all the results presented so far were carried out on a batch mixer. It is believed blending in a TSE would result in finer rubber domains due to higher shear forces. This may lead to an increased improvement in properties.

Thus, there were two goals of the work presented in this chapter: one from the material side and the other from the processing side. On the material side, selected combinations of reactive and non-reactive compatibilizers were explored to evaluate their effectiveness. On the processing side, the blends were prepared in a twin screw extruder (TSE).

Conventional single screw extruders (SSE) are composed of three sections. The polymer pellets or powder are packed in to a solid bed, which is pushed forward, melted and subsequently the melt is pumped through the final flights of the metering section to the die. SSE is usually flood fed and RPM controls the throughput rate. These machines are high pressure machines and their main function is to pump [1]. On the other hand, TSEs have two screws, which either rotate in the same direction (co-rotating) or in opposite directions (counter rotating). The screws may be of intermeshing or non-intermeshing type (Figure 7.1).

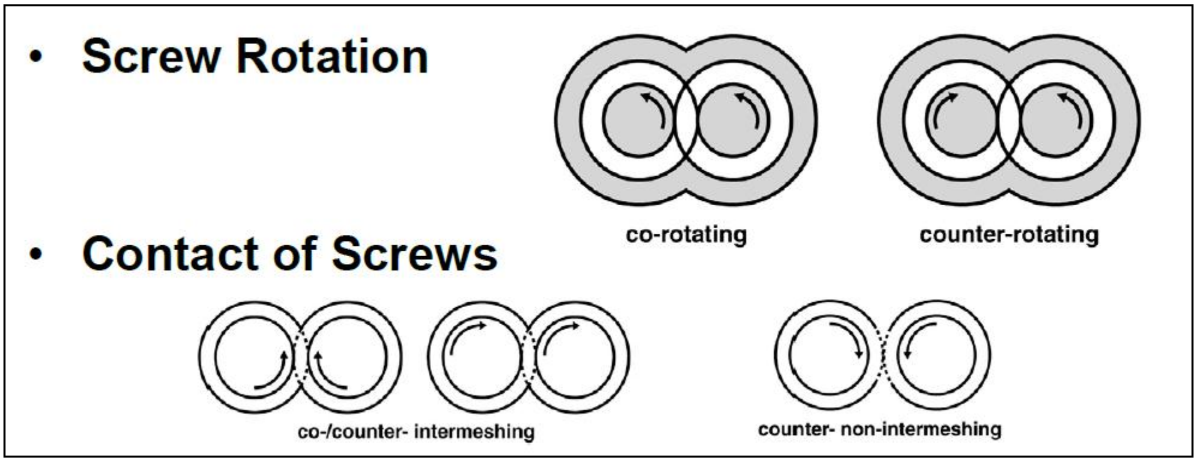


Figure 7.1 Co-rotating (intermeshing and non-intermeshing) and counter-rotating [2]

Rauwendaal [3] performed an experimental comparison of co-rotating and counter-rotating TSEs and observed that the former was superior for distributive mixing, while the latter was superior for dispersive mixing. Flow through high shear regions due to tight clearance between the screws of the counter-rotating screws, was proposed to cause the superior dispersion. TSEs are widely used in the polymer industry for compounding, reactive extrusion and blending, due to their mixing capabilities. The prime reasons TSEs are preferred over SSEs are shorter residence time, improved temperature control, higher shear rates, reduced melt slippage and self-wiping action. TSEs are modular, i.e., the screw configuration can be changed as per the processing requirement by simply re-arranging the screw elements. There are three major types of screw elements (Figure 7.2) – conveying, mixing and zoning.

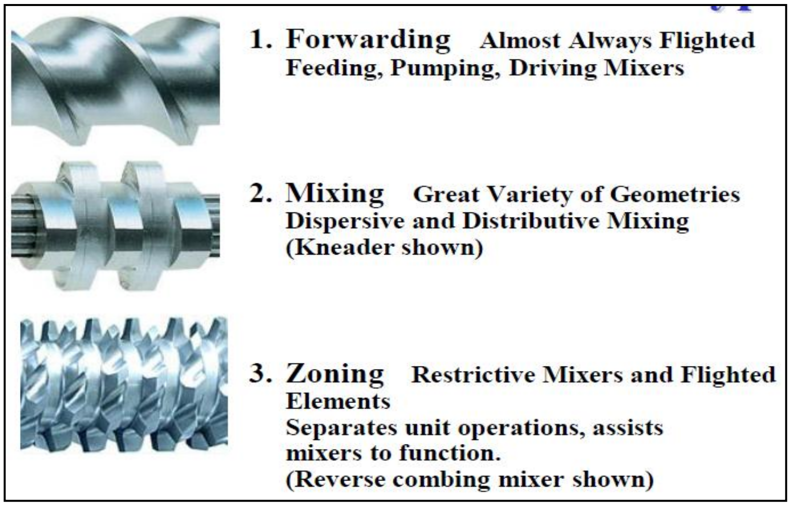


Figure 7.2 Major types of screw elements [2]

Kneading blocks can be arranged so that their conveying efficiency may be altered. Figure 7.3 shows some of the possible arrangements. The forward configuration has greater conveying efficiency than neutral and reverse arrangements. On the other hand, reverse arrangement provides a better shear than the other two configurations. In this project, forward and neutral elements were used in the screw configuration.

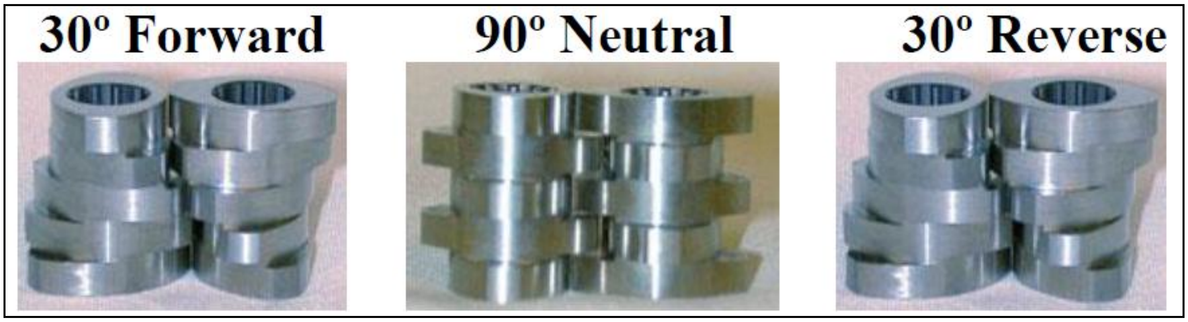


Figure 7.3 Possible arrangements of kneading elements [4]

Various screw elements can be arranged along the length of a screw in such a manner that the required driving and shearing forces are applied on the material. A sample screw configuration is shown here (Figure 7.4). It indicates most of the commonly used screw elements along with their major role.

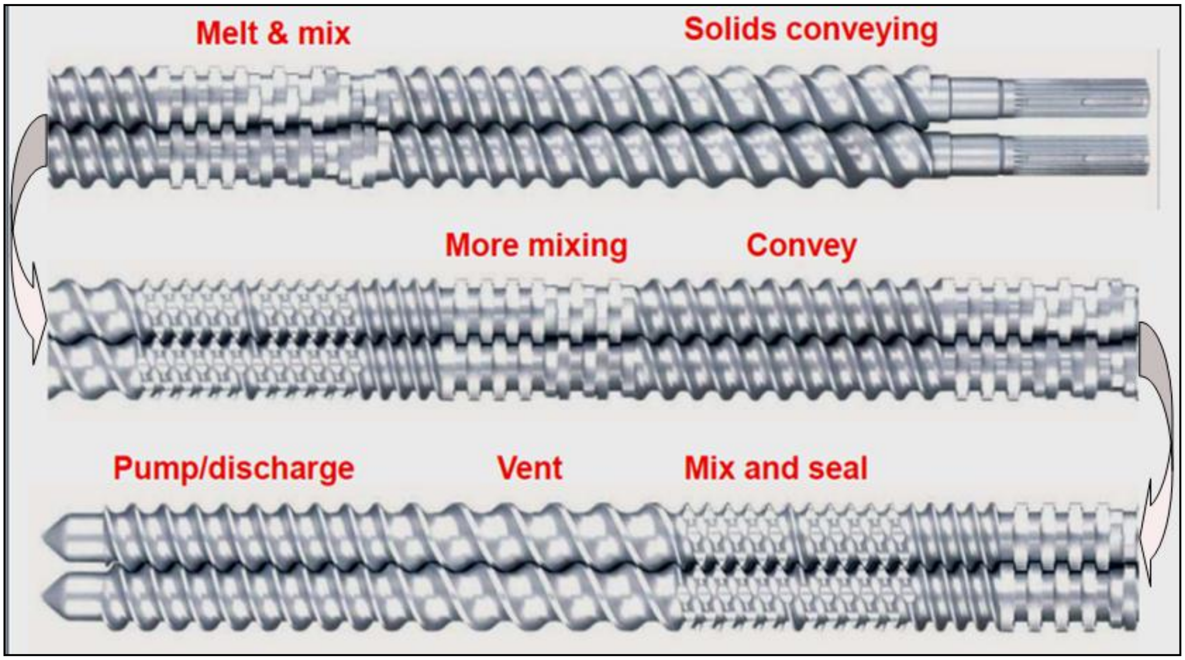


Figure 7.4 A screw configuration showing the various elements and their major function [2]

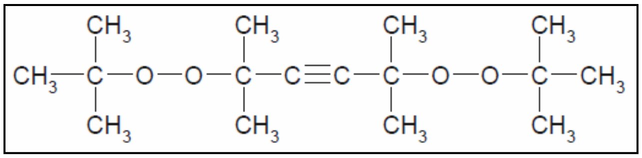
Wider disks provide an increased dispersive mixing, whereas, narrower disks lead to better distributive mixing [5]. Mixing during polymer blending, compounding and reactive extrusion is critical, because the final properties of the polymer depend on the quality of mixing achieved [6]. In their review on mixing of polymers, Ottino and Chella [7] noted that the final properties of a polymer blend depend on the properties of the individual polymers, their compatibility, and the processing conditions, which determine the mixing quality. Mixing can be dispersive or distributive, with the former causing size reduction of the particles and the latter one resulting in the spreading of those particles. Both these types often act simultaneously and are essential to obtain a uniform morphology [8].

Luo and Isayev [9] prepared TPVs from DR produced ultrasonically from 30 mesh GTR coming from tread and sidewalls of passenger and truck tires. The PP used as the plastic phase was Pro-fax 6523 (MFR= 4g/10 mins) from Himont Inc. having a TS of 30 MPa and 12% EB. A curing package based on sulphur and phenolic resin was used to dynamically cure DR (R-GRT). After compression molding, the best properties that could be achieved were around 20% for EB and 9 MPa for TS with PP: R-GRT= 40: 60. The batches made in an internal mixer, performed similarly to or better than those ones produced using TSE. Earlier, Seok and Isayev [10] had prepared PP: GTR= 40: 60 blends, which recorded TS of around 7 MPa and EB of less than 25%.

Li et al. [11] studied the effect of EPDM, DCP, and dimethyl silicone oil on the mechanical properties of HDPE composites filled with 60 mesh scrap rubber powder in an internal mixer. At 60% scrap rubber, the TS (with 10% EPDM, 0.2% DCP, and 4% dimethyl silicone oil) was around 10MPa and EB was 50%. Qin et al. [12] prepared blends using LLDPE (linear low density polyethylene) and GTR (60% by weight). The maximum EB that could be achieved was less than 50% and the maximum TS was 3 MPa. Zhu et al. [13] prepared TPVs from PP (MFR= 1.2g/10 mins) and reclaimed GTR crumbs (80 mesh). Three types of interfacial strengthening agents—degraded PP, hydrosilylated PP, and hydrosilylated PP grafted onto SBR (styrene–butadiene rubber) (10 parts by weight) were blended with PP (40 parts) and 80-mesh rubber crumbs (50 parts) in a batch mixer. The maximum TS obtained was 12 MPa and EB was less than 50%.

Naskar et al. [14] prepared rubber-plastic blends, wherein the rubber phase consisted of a mixture of EPDM and GTR. The plastic phase consisted of acrylic-modified high density polyethylene (A-HDPE). DCP was added to carry out the dynamic vulcanization in an internal mixer. Without EPDM, GRT: A-HDPE= 60: 40 gave 5 MPa TS and 43% EB. Upon addition of EPDM, the blend of EPDM: GRT: A-HDPE= 15: 60: 25 gave TS of 6.5 MPa and 155% EB. Kumar et al. [15] prepared ternary blends using GTR (particle size 0.4-0.7mm), LDPE (Lupolen 1840 H) and fresh rubber with and without dynamic vulcanization. The composition was fixed to LDPE: GTR: Fresh rubber= 50: 25: 25 with each of the virgin rubbers- SBR, NR and EPDM. Maximum TS that could be achieved was less than 6 MPa and the maximum EB was approximately 60%. Liu et al. [16] prepared TPVs using recycled EPDM and PP (MFR 0.75 and 12). t-Butyl hydroperoxide was used to carry out dynamic vulcanization in an internal mixer. At 80% rubber content the TS was less than 5MPa and EB was less than 100%.

Thus, there have been numerous attempts to prepare TPVs from GTR and plastics. The EB achieved in the past using up to 60% DR was only 25%, which is not useful for commercialization purposes [9]. This chapter describes the results achieved using DRT and PP in a TSE with a combination of compatibilizers and curatives. As DRT was found to be more responsive to the reactive blending techniques than DRE, the work on TSE was carried out using DRT. Engage® 8200 and Polybond® 3200 were chosen as the compatibilizers to use with the curatives because of their structural similarity with PP, which was thought to help improve the compatibility with PP phase. Additionally, Polybond is known to contain unsaturation, which may enable it to interact with COOH and CHO groups that are produced on rubber molecules when subjected to oxidative degradation (during the grinding process). Two other peroxides– Trigonox® 145-E85 (2, 5-Dimethyl-2, 5- di (tert-butylperoxy) hexyne-3) and Trigonox® 311 (2, 5-Dimethyl-2, 5-di(tert-butylperoxy) hexyne-3) were tested. Trigonox® 145-E85 (Tx-145) is a bifunctional peroxide. Trigonox® 311 (Tx- 311) has a typical crosslinking temperature above 200°C. The chemical structures of Tx 145 and Tx 185 are shown in Figure 7.5.



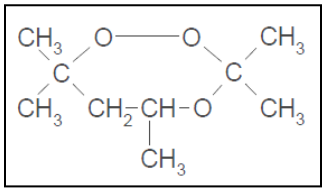


Figure 7.5 Structures of Tx-145 and Tx-311

7.2 Experimental

7.2.1 Materials

PP (PH382M) had a MFR of 3.5 g/10 min, TS of 35 MPa and EB of 10%. DRT was produced from tire buffing and upon curing with sulphur package (S 1.5, TBBS 1.5, ZnO 3, St. A 2 phr) showed a TS of 11.2 MPa and EB of 223%. Engage® 8200 (ENG) and Polybond® 3200 (PBD) were used as compatibilizing resins. DCP, Tx 145 and Tx 185 were used for crosslinking. It should be noted that peroxide based curing package contained DCP, unless mentioned otherwise. Sulphur was used as a coagent for DCP wherever required. Staining of the samples for SEM analysis was carried out using osmium-tetraoxide.

7.2.2 Experimental design

Typically TPOs/ TPVs contain around 70% rubber, and given that the main goal of the project was to explore application of DRT, additional experiments and characterizations were performed on blends with DRT content of at least 70%. Moreover, EB values closer to that of typical TPOs/ TPVs blends (100% EB) were so far displayed only by blends having high rubber content (80%), and hence it seemed logical to focus on the blends with high rubber content. ENG and PBD were added to the blends as compatibilizers at a weight percentage of 10% (at least) for each of them. ENG is a TPE and hence, it was thought to replace parts of DRT. On the other hand, PBD being a functionalized PP was considered as a part of PP wherever used.

A full DOE could not be carried out due to various constraints of the processing variables. For instance, at a low screw RPM, the range for varying the resin feedrate was very limited. A lower resin feedrate implied a much lower feedrate of curatives (2% by weight), which induced inconsistency in the flow of curatives due to feeder limitations. On the other hand, a lower screw speed also limited the maximum resin feedrate in order to avoid material flooding at the hopper. Considering these constraints, various variables such as dosage of curatives, screw speed, type of curatives etcetera were studied as single factor experiments at fixed other conditions of experiments. Reference samples, without any compatibilizers, were prepared in order to compare the properties.

7.3 Results and Discussion

7.3.1 Blends with Rubber: PP= 80: 20

Tensile Properties

Effect of composition

Two-component blends (DRT: PP= 80: 20): Blends consisting of DRT and PP, without any compatibilizers, are referred to as two-component blends. Similar to earlier work in the batch mixer, blends were prepared consisting of DRT and PP (DRT: PP= 80: 20) in the TSE, and were tested with and without the addition of curatives at fixed conditions (resin feed rate 37.5 g/min and screw speed 100 RPM). Figure 7.6 shows the TS and EB obtained for DR: PP= 80: 20 blends. It can be seen that addition of curatives (2% DCP) increased the TS and EB; however, the EB obtained still is not adequate for commercial applications.

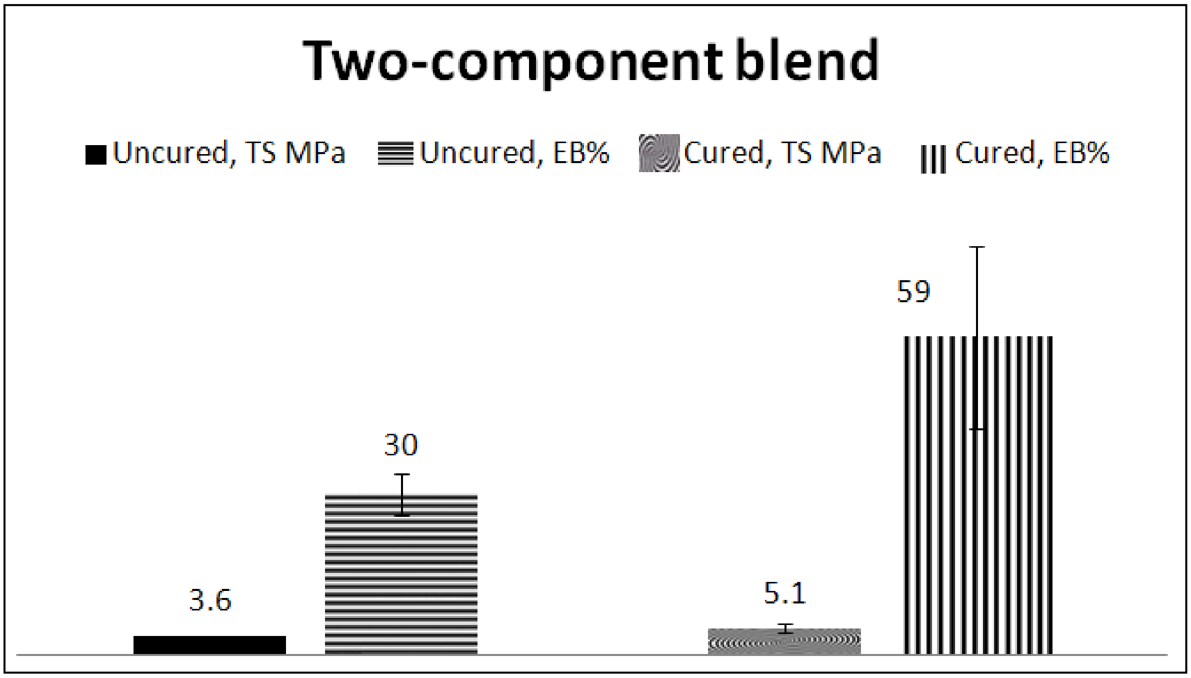


Figure 7.6 TS and EB of cured and uncured DRT: PP= 80: 20

Blends made from DRT, PP along with compatibilizers: The properties obtained for various combinations are shown in Table 7.1. ENG and PBD were added individually and together to evaluate their effects. It is seen that addition of the ENG and PBD together at the same conditions along with curatives led to the highest increase in EB and TS (more than 100% EB). Also, it was noticed that lowering the screw RPM further improved the properties of the blends (up to 150% EB). This is attributed to the residence time, which is elaborated in the next section. Reproducibility of the sample was quite good, which confirms the improvement in properties. Replacement of some DRT with 20% ENG produced even better properties (195% EB), but because ENG is a costly material, this approach was not explored further.

Table 7.1 Properties of various blends (resin feed rate 37.5 g/min)

Compositions	**DCP Dosage (%)**	**Screw RPM**	**TS (MPa)**	**EB (%)**
DRT: PP= 80: 20	0	250	2 ± 0.4	10 ± 5
DRT: PP= 80: 20	2	250	2.8 ± 0.2	45 ± 10
DRT: ENG: PP= 70:10:20	0	250	2.4 ± 1	34 ± 16
DRT: ENG: PP= 70:10:20	2	250	4.1 ± 0.5	38 ± 10
DRT: PBD: PP= 80:10:10	0	250	3.3 ± 0.2	40 ± 6.4
DRT: PBD: PP= 80:10:10	2	250	5.4 ± 0.8	57 ± 17
DRT: ENG: PBD: PP =70:10:10:10	2	250	7.4 ± 0.7	115 ± 18
DRT: ENG: PBD: PP =70:10:10:10	2	100	10.2 ± 0.4	150 ± 8.5
DRT: ENG: PBD: PP =70:10:10:10 (*reproduced*)	2	100	10.6 ± 0.3	165 ± 10
DRT: ENG: PBD: PP =60:20:10:10	2	100	9.2 ± 0.7	195 ± 24

Stress-strain curves of compositions given in Table 7.1 are shown in Figure 7.7, and Figure 7.8 enlarges the circled portion of Figure 7.7 in order to clearly visualize the properties of the blends with low EB. The plot for DRT: ENG: PBD: PP= 70: 10: 10: 10 is for the sample made at 100 RPM. When added individually, addition of PBD produced better results than ENG at the same dosage. However, the combination of the two significantly improved the properties.

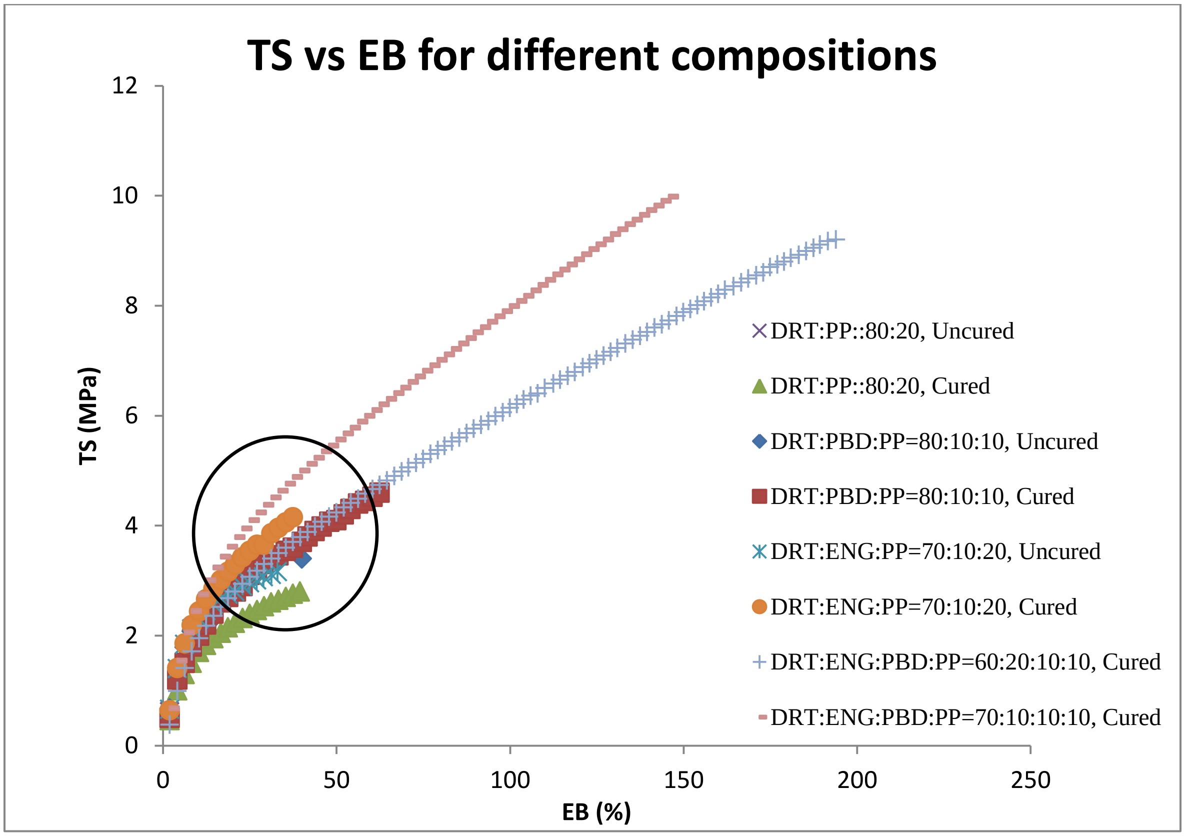


Figure 7.7 TS versus EB plots for various compositions (circular region zoomed in Figure 7.8)

It seems that the PBD helps in forming a good interphase between PP and DRT. As PBD has a structure similar to PP, it can interact and co-crystallize with PP and on the other hand, it has double bonds, which help it participate in reactions with the rubber phase. Thus, it acts as a binder for the PP molecules. It is proposed that ENG, being a TPE, may be blending well with DRT and that apart, having PE units in the backbone may be helping it to interact with PP molecules due to the similarity in the chemical structure.

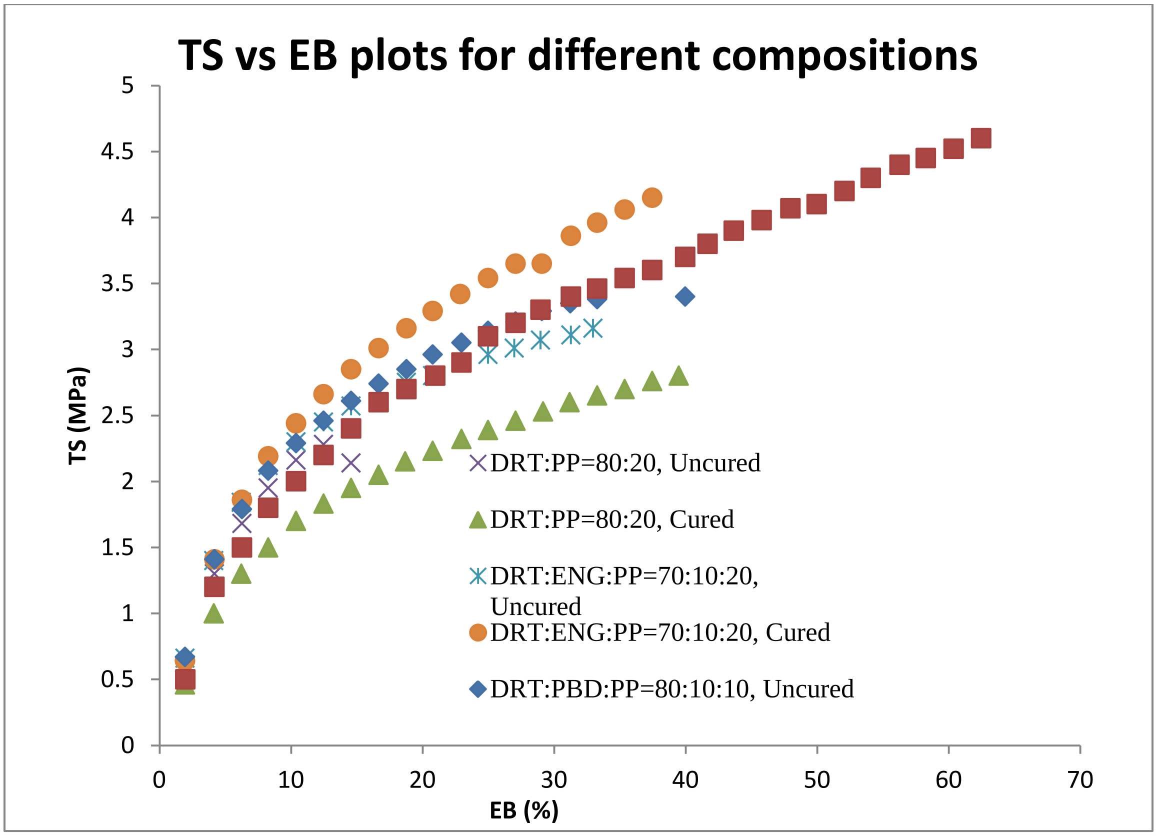


Figure 7.8 TS versus EB plots for various compositions having at least 70% DRT
(Values may differ slightly from Table 7.1 as the table gives an average value)

Figure 7.9 compares the properties of the DRT: ENG: PBD: PP= 70: 10: 10: 10 blend (referred to as four-component blend) in the presence and absence of curatives produced at a 100 RPM screw speed and a feedrate of 37.5 g/min. From the results, it is evident that the presence of curatives is essential to achieve good properties. After a series of experiments, this combination of screw speed and feedrate (referred to as ‘condition A’) was found appropriate to achieve good samples.

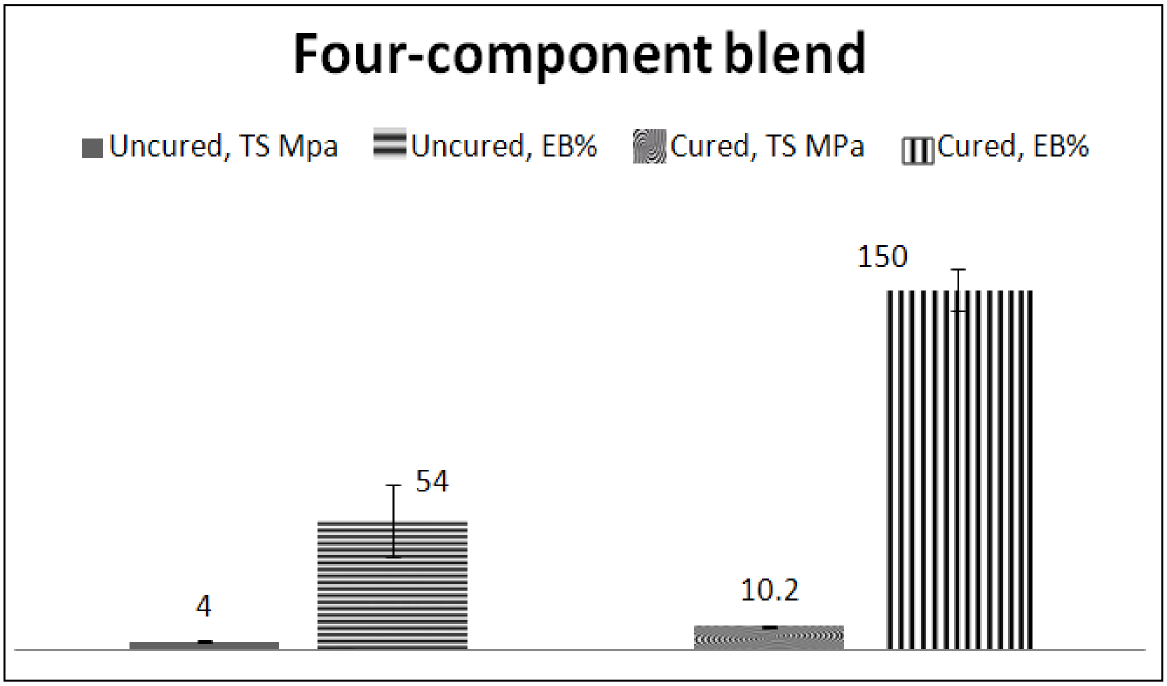


Figure 7.9 TS and EB of cured and uncured DRT: ENG: PBD: PP= 70: 10: 10:10

Effect of Residence Time

Residence time is defined as the time taken by a fluid element to pass through the extruder and come out of the die. This is an average value as different elements would take various paths and hence, there would be a set of residence times (residence time distribution). A faster screw speed, would lead to lesser residence time. It is expected that better properties are achieved when enough residence time is provided so that the crosslinking reactions induced by the curing system are completed. To test this possibility, the screw RPM was varied over five levels keeping all other parameters constant (condition A), and the effects on TS and EB were evaluated (Figure 7.10 and Figure 7.11).

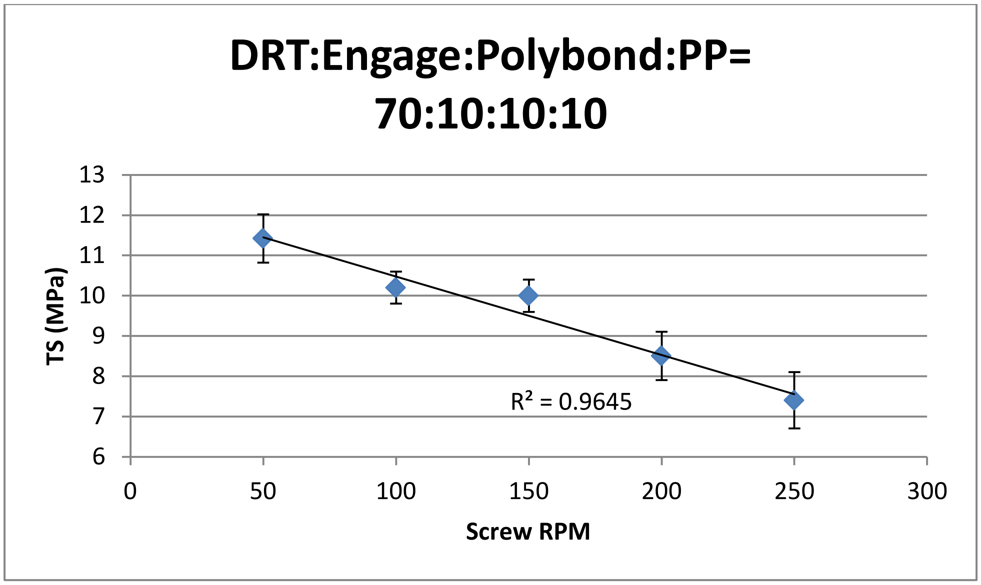


Figure 7.10 Effect of screw RPM on TS

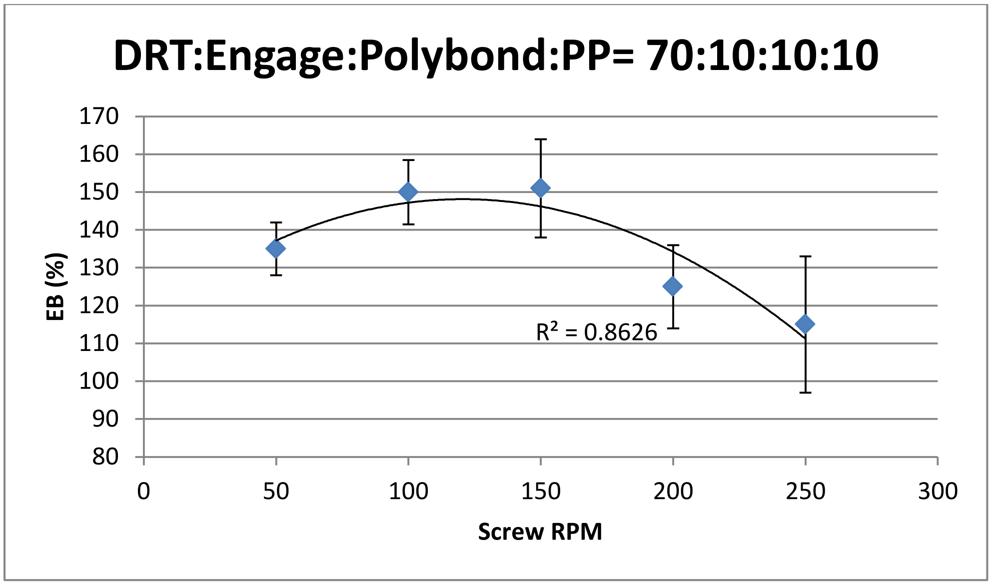


Figure 7.11 Effect of screw RPM on EB

It was found that 100 to 150 RPM provided sufficient residence time for the reactive compatibilization to complete. Beyond 150 RPM, possibly due to the lack of residence time, the compatibilization reactions are not completed and hence, the properties deteriorated.

Another reason may be that at high shear rates, the material is over-sheared, which resulted in degradation of the material.

Effect of DCP dosage

Curing dosage was varied across three levels and the results are shown in Figure 7.12 and Figure 7.13. It was found that 2% was a sufficient dosage to get optimum properties. It may be the case that at 3%, degradation reactions become prominent and hence, the TS value does not increase. On the other hand, a dosage of 1% was not enough to carry out sufficient crosslinks between the rubber and plastic phases. Considering the standard deviations, EB was the same for 2% and 3% DCP. Therefore, 2% seemed as an optimal amount to allow for sufficient curing.

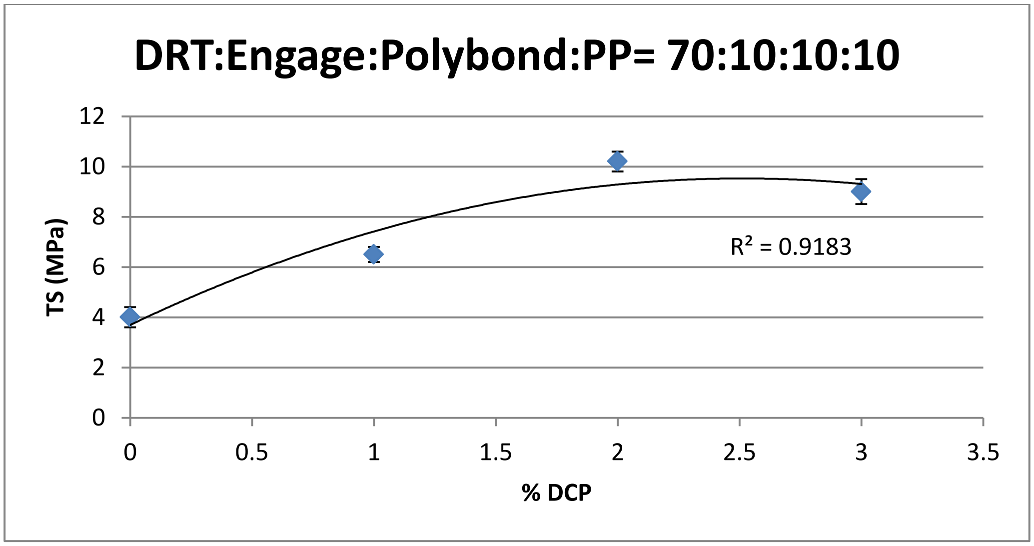


Figure 7.12 Effect of curing dosage on TS

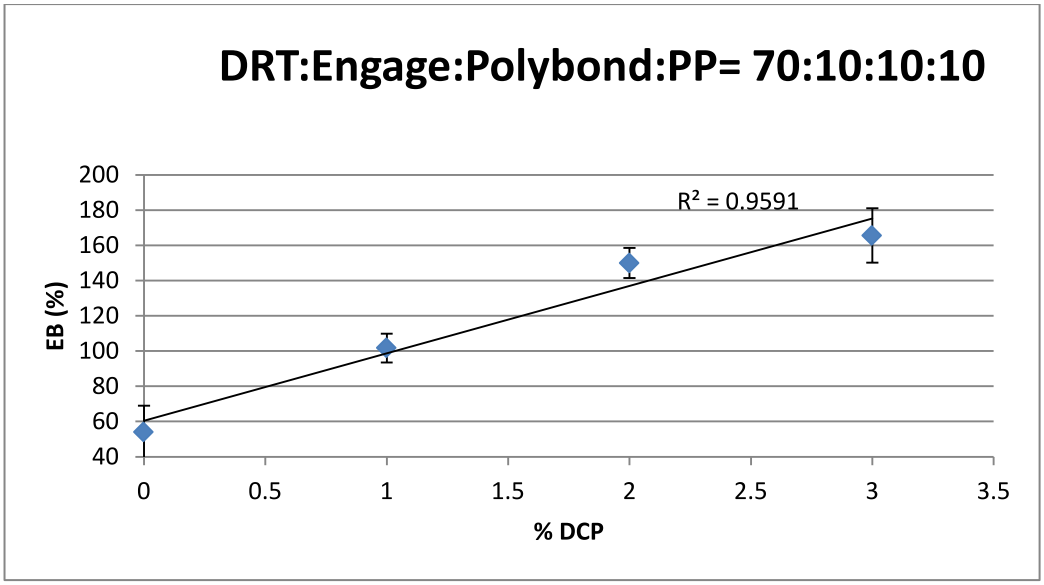


Figure 7.13 Effect of curing dosage on EB

Type of Peroxide

Properties obtained by using three types of peroxides are shown in Table 7.2. It was found that Trigonox® 145 (Tx 145) was more effective and Trigonox® 311 (Tx 311) was least effective in improving the properties among the three peroxides used. The improved performance of Tx 145 may be due to its bi-functional nature in addition to the fact that Tx 145 can produce a greater number of radicals for a given concentration. This allows it to get involved in more crosslinking reactions, which may have led to the formation of a better interphase. In the case of Tx 311, it may have happened that the dosage was not sufficient. However, as the study of peroxides was out the scope of the work, the subject is left for future studies.

Table 7.2 Effect of different peroxides

Compositions	Peroxide type (at 2% dosage)	TS (MPa)	EB (%)	Modulus at 100% (MPa)
DRT: ENG: PBD: PP = 70:10:10:10	DCP	10.2 ± 0.4	150 ± 8.5	7.9
DRT: ENG: PBD:PP = 70:10:10:10	Tx 145	9.9 ± 0.3	182 ± 7	6.6
DRT: ENG: PBD:PP = 70:10:10:10	Tx 311	3.1 ± 1.2	40 ± 20	--

-- Could not be obtained

Hardness and Compression Set

Table 7.3 shows compression set and hardness values for these compositions. The values are similar for two-component blends considering the high standard deviations. More readings are required to reduce the standard deviations. Compression set was higher for the uncured four-component blend. This is expected because ENG, which was used to replace DRT, being a TPE has inherently higher set values than DRT. Crosslinking is known to improve the set properties and accordingly, it was noticed that upon addition of curatives the set value decreased to around 40%. This is an acceptable value for general purpose TPV applications.

It was expected that curing would increase the hardness values. However, only a slight increase in hardness values upon curing was recorded, and all the samples had hardness values in the range of 80- 85 Shore A. This may be due to the presence of rubber crumbs in the material, which being already crosslinked contributed towards increased hardness values.

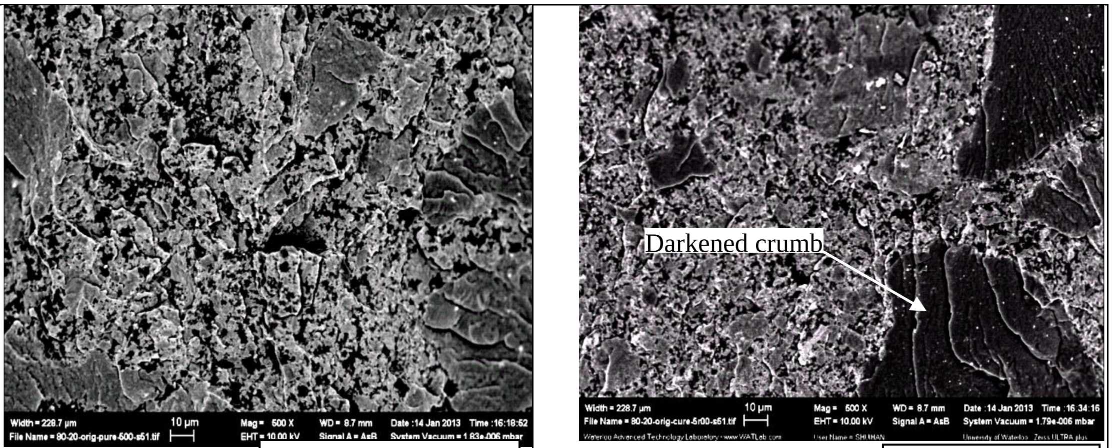
Table 7.3 Compression set and hardness values for various TPOs/ TPVs

	Compression Set (%)	**Hardness (Shore A)**
DRT: PP= 80: 20, Uncured	42.25 ± 7.4	82 ± 0.7
DRT: PP= 80: 20, Cured	42.6 ± 1.7	84 ± 0.5
DRT: ENG: PBD: PP= 70:10:10:10, Uncured	58 ± *	81 ± 0.8
DRT: ENG: PBD: PP= 70:10:10:10, Cured	40 ± 3	85 ± 0.3
DRT: ENG: PBD: PP= 70:10:10:10, Cured (Tx 145)	47.9 ± 2	83 ± 0.2

* Only one reading could be taken

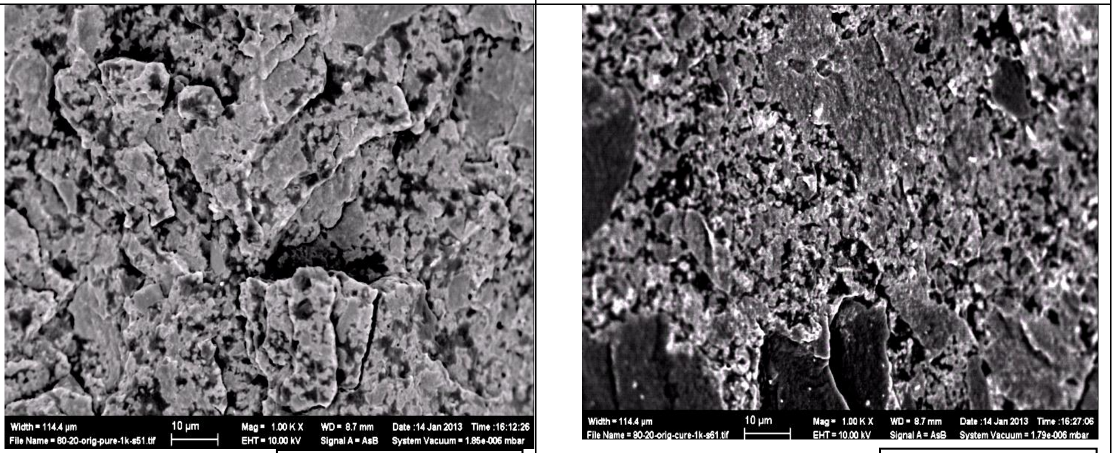
Morphology

Figure 7.14 and Figure 7.15 show the morphology of cured and uncured two-component and four-component blends. It is observed that in case of the uncured sample (A), the rubber crumbs are brighter. Addition of curatives resulted in darker rubber crumbs probably due to the disappearance of their double bonds. Hence, curing resulted in a better interphase between the matrix and rubber crumbs. This may be the reason behind the better properties achieved. Similar observations were made in four-component blends as well.



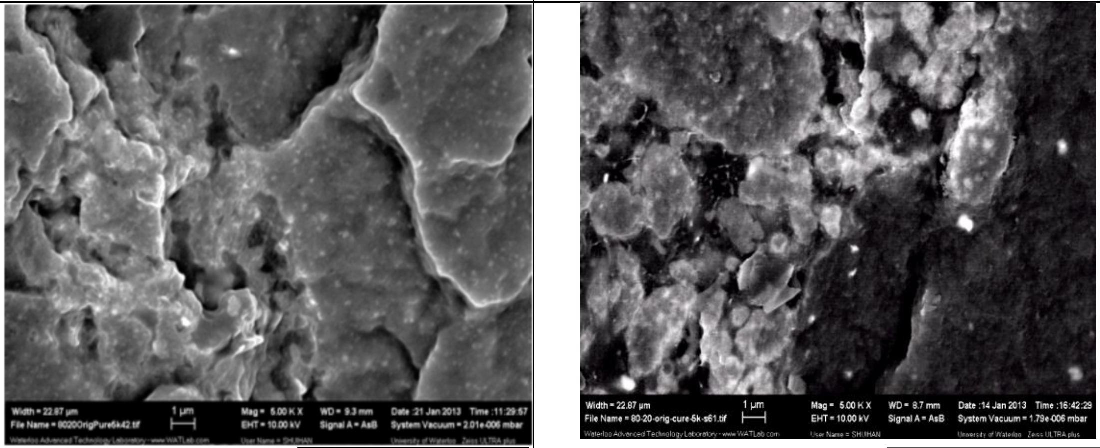
A.Uncured-500X

B.Cured-500X



C.Uncured-1kX

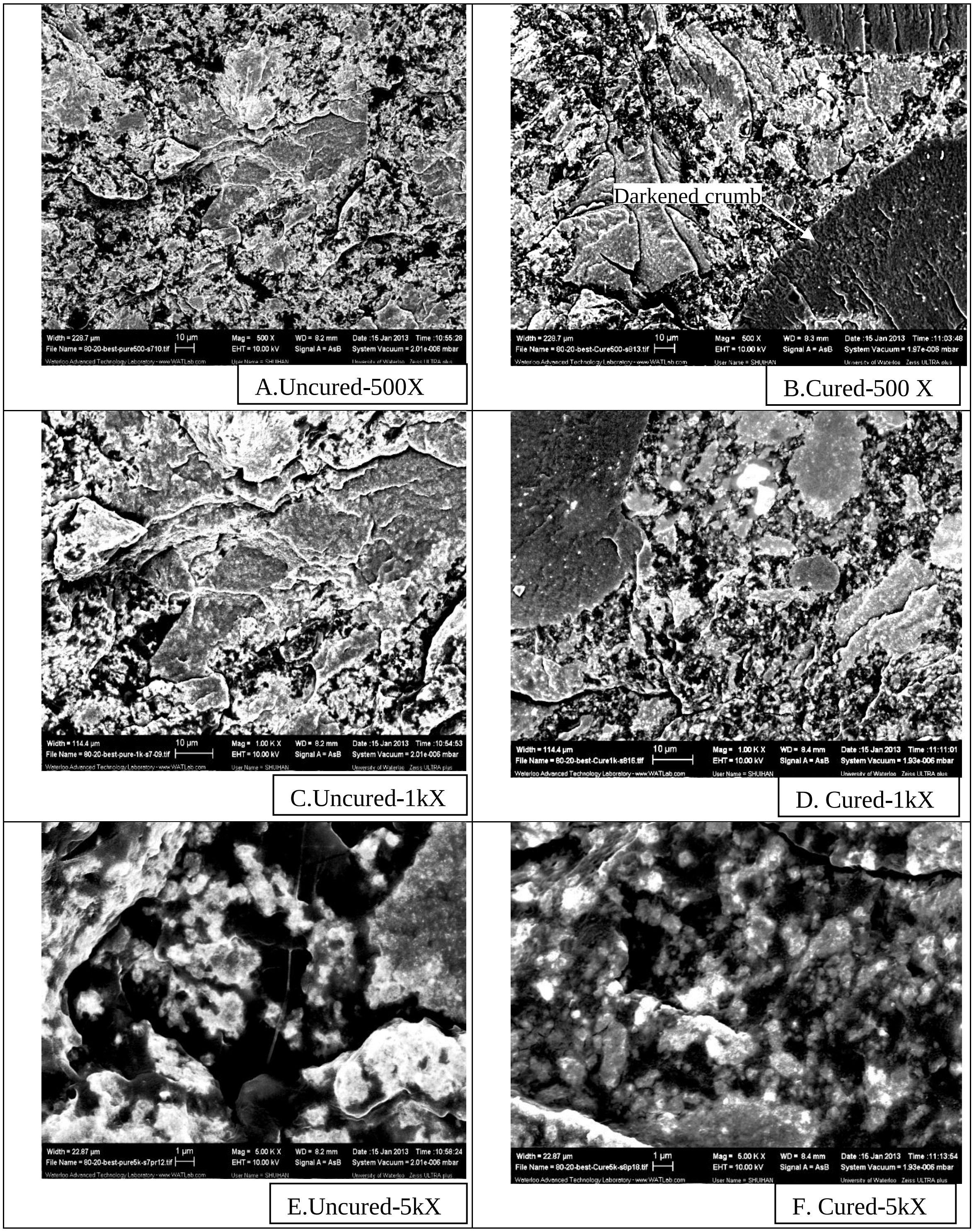
D.Cured-1kX



E.Uncured-5kX

F. Cured-5kX

Figure 7.14 SEM pictures for sample DRT: PP= 80: 20, Uncured and DCP cured



A.Uncured-500X

B.Cured-500 X

C.Uncured-1kX

D. Cured-1kX

E.Uncured-5kX

F. Cured-5kX

Figure 7.15 SEM pictures for DRT: ENG: PBD: PP= 70: 10:10:10, Uncured and DCP cured

SEM pictures were taken for Tx-145 cured samples (Figure 7.16) as it gave improved properties compared to DCP and Tx-311 cured samples. The rubber crumbs reduced in size and showed a thicker interphase than DCP cured samples (distinguishable at 5kX images).

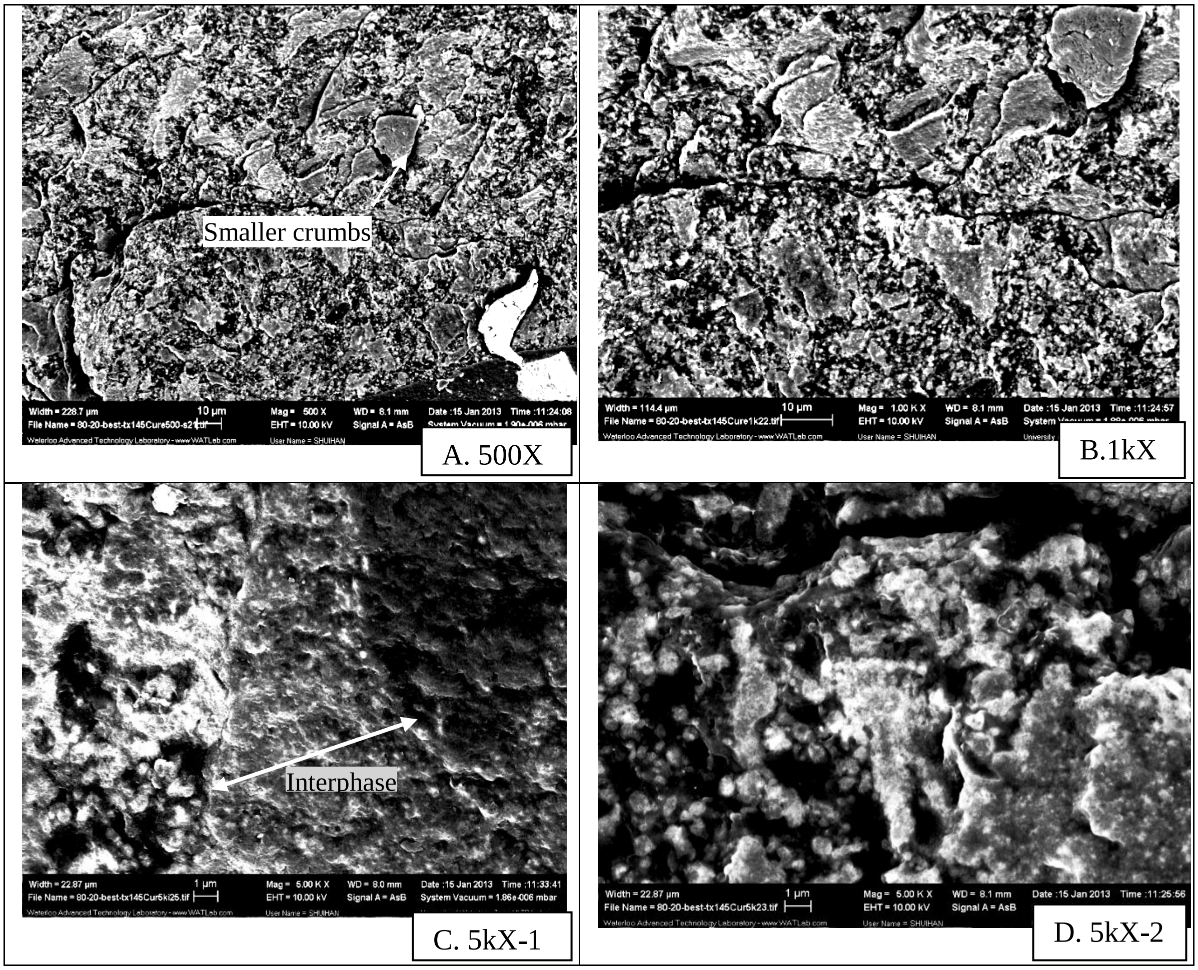


Figure 7.16 SEM pictures of DRT: ENG: PBD: PP= 70:10:10:10 blends, Tx 145 cured

DSC Analysis

Table 7.4 tabulates the MP and degree of crystallinity values as measured using DSC. It can be seen that addition of curatives leads to a decrease in MP, and in all cases is accompanied with a reduction in degree of crystallinity. This trend is expected because crosslinking makes it difficult for the chains to crystallize.

Table 7.4 Melting point and degree of crystallinity of various TPOs/ TPVs

Composition	Melting point (°C)	Degree of crystallinity (%)
DRT:PP= 80:20, Uncured	163.2	36.5
DRT:PP= 80:20, DCP Cured	158.8	30.8
DRT: ENG: PBD: PP= 70:10:10:10, Uncured	162.8	38.6
DRT: ENG: PBD: PP= 70:10:10:10, DCP Cured	159.2	32.2
DRT: ENG: PBD: PP= 70:10:10:10, Tx 145 Cured	158.8	27.8

Soluble Content

It was seen that upon curing, as expected, the percentage soluble (sol.) content was reduced (Table 7.5). This is associated with the formation of crosslinks between and within the two phases. Four-component uncured blend had lower sol content than two-component uncured blend, which suggests that even in uncured form, the phases have relatively better interaction. Standard deviations were 0.1, 0.1, 0.2 and 0.27 for %acetone extractable,

%toluene extractable, %xylene extractable and %sol respectively. Cured four-component blends, which showed the better properties, have markedly lower soluble content, hinting at a high crosslink density and compatibilization.

Table 7.5 Percentage soluble content of blends

Composition	Acetone extractable (AE) %	Toluene extractable (TE) %	Xylene extractable (XE) %	% Sol (TE + XE)
DRT:PP:: 80:20, Uncured	3.03	5.29	11.86	17.2
DRT:PP:: 80:20, DCP Cured	2.65	2.41	9.49	11.9
DRT: ENG: PBD: PP= 70:10:10:10, Uncured	2.44	7.25	6.32	13.6
DRT: ENG: PBD: PP= 70:10:10:10, DCP Cured	2.15	1.41	6.72	8.1
DRT: ENG: PBD: PP= 70:10:10:10, Tx-145 Cured	2.55	2.02	7.11	9.13

Rheology

As expected, DCP cured blends showed higher viscosity at all shear rates as compared to the uncured blends, which may be due to improved interaction between the rubber and plastic phases (Figure 7.17). However, it was noticed that the Tx-145 cured sample showed a viscosity value lying between that of the uncured and DCP cured blends. In fact, at higher shear rates, the Tx-145 cured samples had a viscosity similar to that of the uncured blends. This suggests that a different kind of molecular interaction is present in the Tx 145 cured samples. The presence of 15% mineral oil in Tx 145 may have led to the reduction in the blend viscosity.

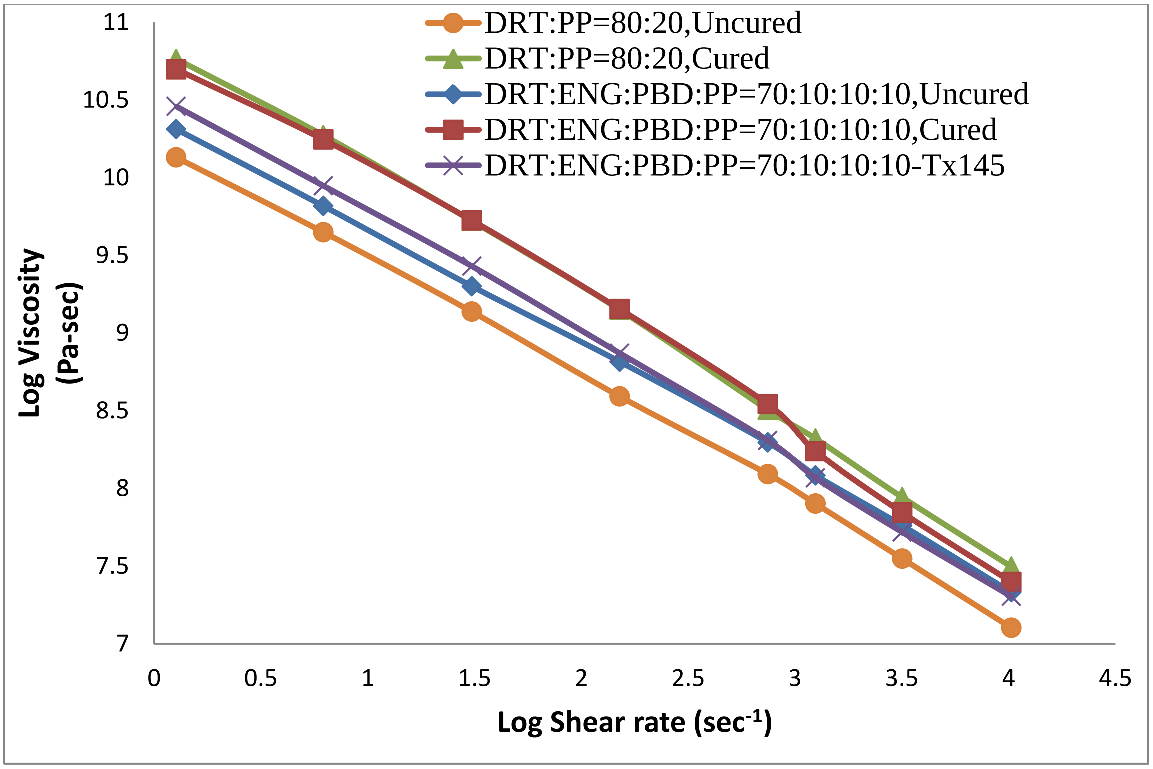


Figure 7.17 Viscosity versus shear rate plots at 200°C for various compositions

7.3.2 Blends with Rubber: PP= 60: 40

Tensile Properties

Two-component blends (DRT: PP= 60: 40)

Addition of curatives increased both the TS and EB, although EB showed a higher increase upon curing than TS (Figure 7.18). The curative package consisted of DCP: Sulphur= 1: 1 at a total of 4% dosage (deduced as the appropriate combination from previous experiments). The role of sulphur was to stabilize tertiary PP radicals and form sulphur bridges in order to improve interfacial adhesion. The significant increase in EB indicates that a better compatibility was achieved with curatives.

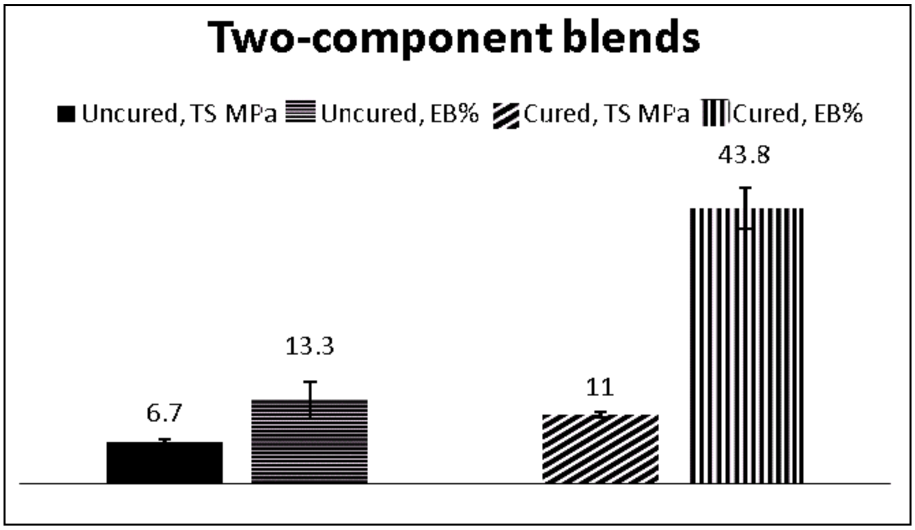


Figure 7.18 TS and EB for two-component blend of DRT: PP= 60:40

The same composition, when mixed in a batch mixer with our curatives, gave a TS of 5.8 (± 0.3) MPa and an EB of 11.7 (± 2.4) %. Upon curing, a TS of 13.2 (± 1) MPa and an EB of 34.7 (8.6) % was achieved. Thus, it was found that batch mixer and TSE provided similar results. This may be due to the presence of rubber crumbs. It seems that because these crumbs are already crosslinked, they are tough enough to withstand the high shear forces in a TSE and hence, remain intact as in the case when mixed in a batch mixer. Those crumbs act as stress concentrators and therefore, no significant improvement in properties is evident when using a TSE in place of a batch mixer.

Four-component blends (DRT: ENG: PBD: PP= 50: 10: 10: 30)

In the case of four-component blends too, TS and EB responded positively to the curing system (Figure 7.19). A comparison of the uncured and cured two-component and four-component blends shows that addition of compatibilizers resulted in similar properties. This was not the case for rubber: plastic= 80: 20 blends, where cured four-component blends performed far better than other compositions. This may be due to increased dosage of PP because of which PBD and ENG could not effectively compatibilize PP and DRT. If this possibility is true, then addition of more PP should further decrease the properties. This shall be analyzed later in the chapter.

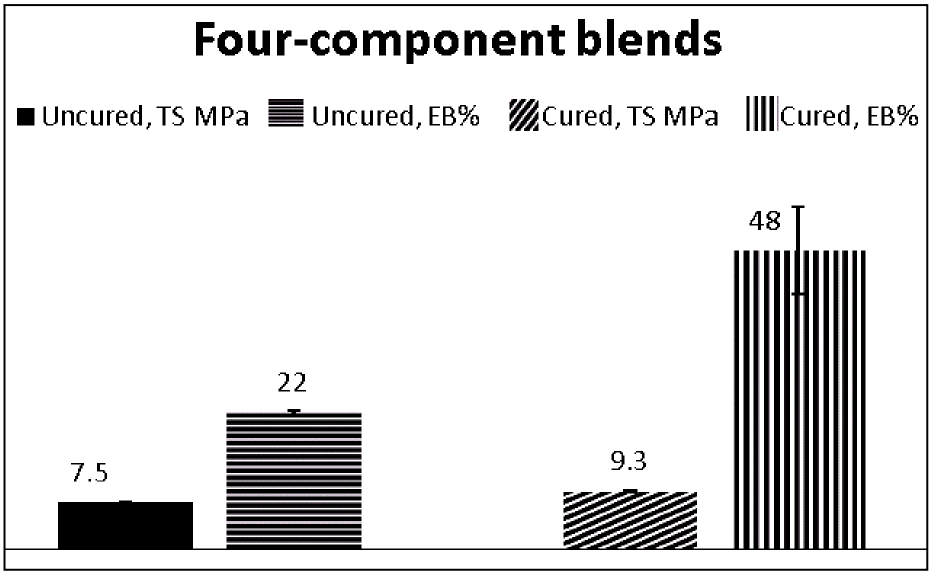
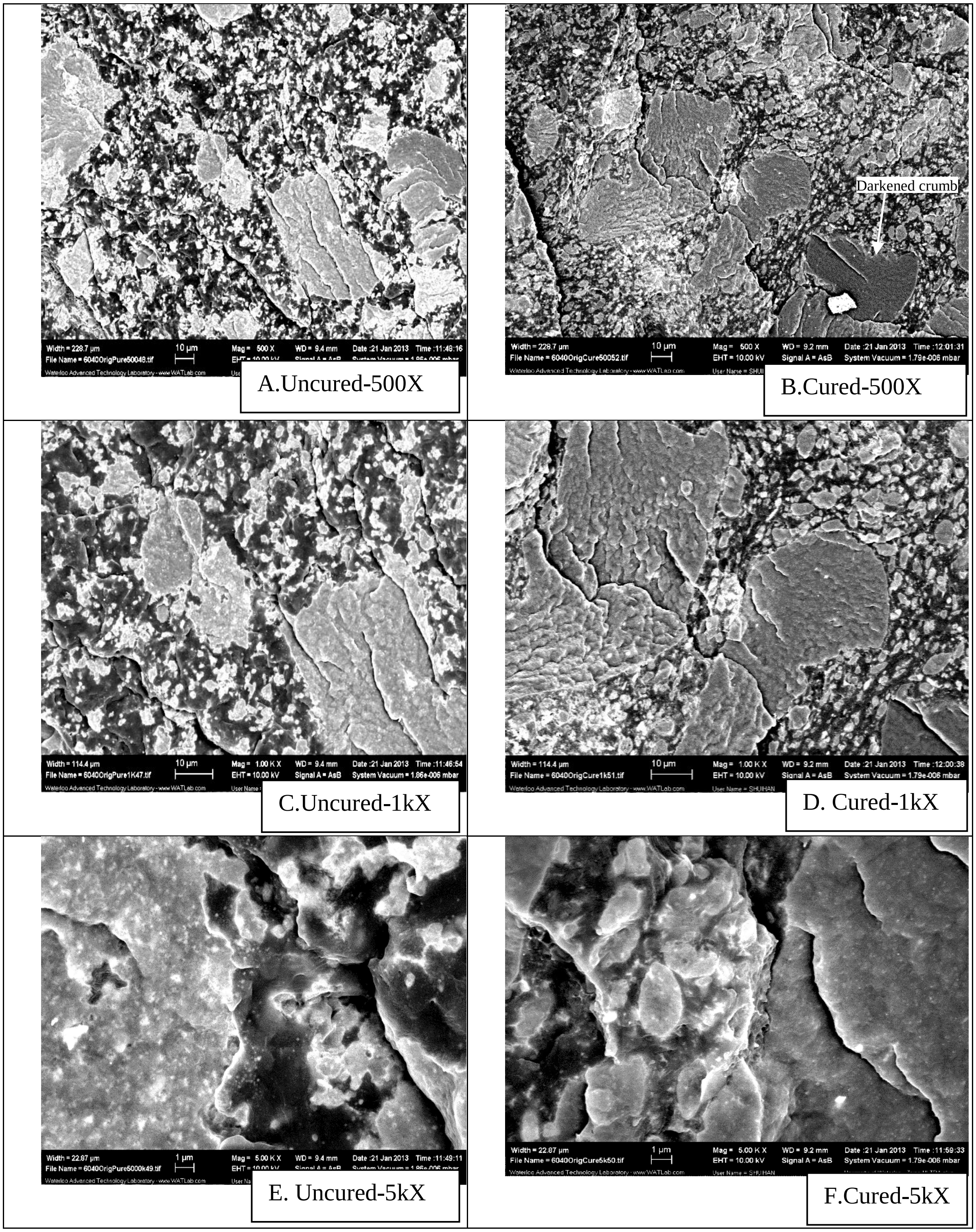


Figure 7.19 TS and EB for four-component blends, DRT: ENG: PBD: PP= 50: 10: 10: 30

Morphology

Figure 7.20 and Figure 7.21 show the morphology of the two-component and four-component blends respectively. It can be observed that the cured blend showed darker rubber crumbs indicating that the double bonds in the crumbs have reacted. As this is accompanied with an increase in EB, it may be assumed that the crumbs have also participated in the reactions with the matrix phases. Also, the rubber domains seemed more discrete and well dispersed in the cured blends. Thus, addition of curatives led to a better interfacial adhesion of the crumbs with the matrix and smaller rubber domains, which resulted in improved properties.



A.Uncured-500X

B.Cured-500X

C.Uncured-1kX

D. Cured-1kX

E. Uncured-5kX

F.Cured-5kX

Figure 7.20 SEM pictures of DRT: PP= 60: 40 blends

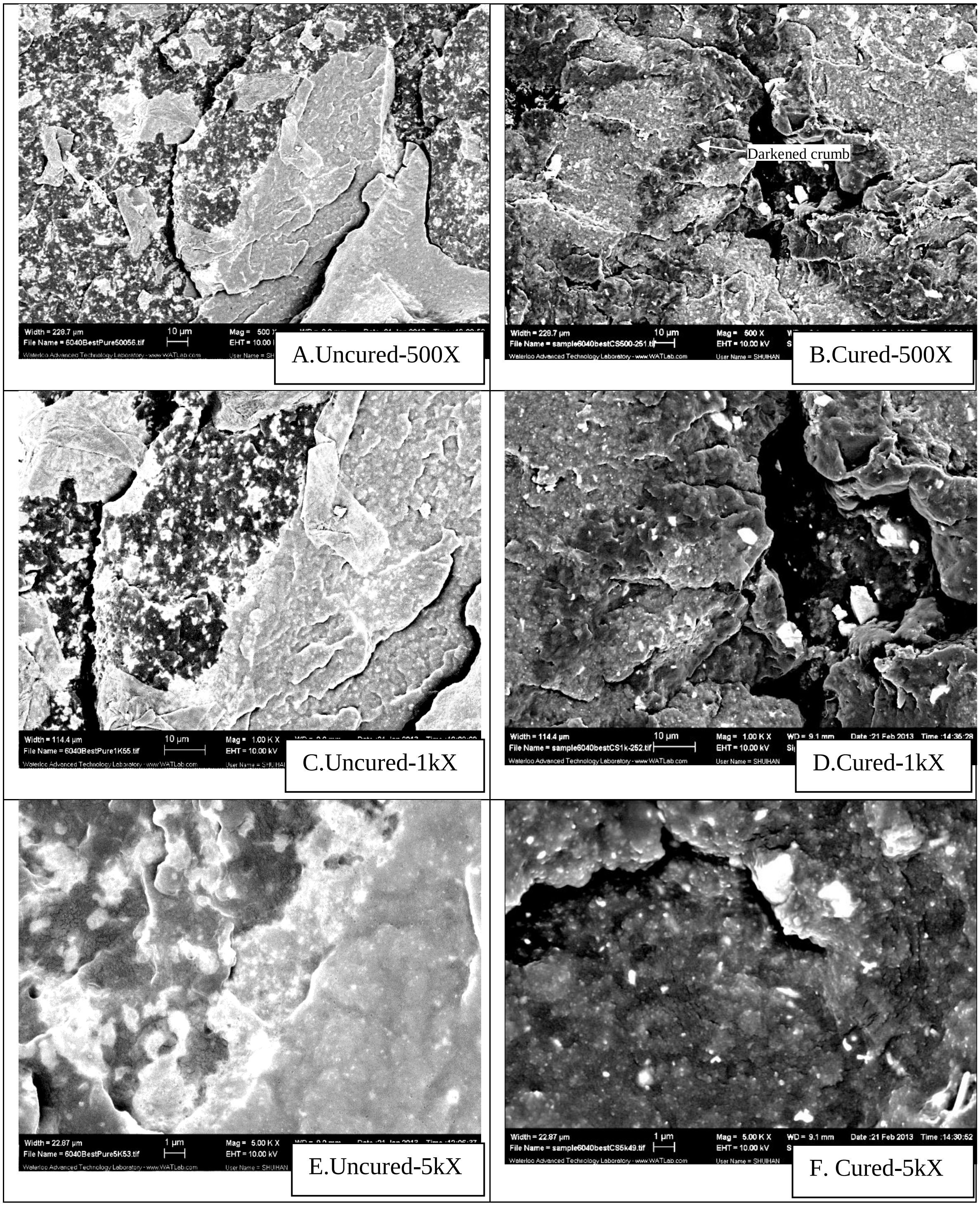


Figure 7.21 SEM pictures of four-component blends (DRT: ENG: PBD: PP= 50: 10: 10: 30)

DSC Analysis

DSC results indicated a drop in the degree of crystallinity and MP, upon addition of curatives (Table 7.6). This trend, which indicates an increase in compatibility, was also seen with the blends having 80% rubber, although the decrease in melting points was more significant than the case here. The reasons for such a trend have already been elaborated in the earlier chapters.

Table 7.6 DSC results for Rubber: PP= 60:40 blends

Composition	Melting point (°C)	Degree of crystallinity (%)
DRT: PP= 60: 40, Uncured	164.5	38.4
DRT: PP= 60: 40, Cured	162.3	27.4
DRT: ENG: PBD: PP= 50:10:10:30, Uncured	162.6	38.9
DRT: ENG: PBD: PP= 50:10:10:30, Cured	161.2	30.9

Soluble Content

As seen in Table 7.7, sol content decreased with addition of curatives. This trend is similar with the one noted for the Rubber: Plastic= 80: 20 blends. It reinforces the idea that curatives help in forming a more coherent material by inducing crosslinks. The cured two-component and four-component blends showed similar properties and the same was true for their sol contents too.

Table 7.7 Soluble content for Rubber: PP= 60:40 blends

Composition	Acetone extractable (AE) %	Toluene extractable (TE) %	Xylene extractable (XE) %	% Sol (TE + XE)
DRT:PP= 60:40, Uncured	1.93	4.30	16.18	20.5
DRT:PP= 60:40, Cured	2.18	3.0	7.13	10.1
DRT:ENG:PBD:PP= 50:10:10:30, Uncured	0.08	7.19	18.08	17.2
DRT:ENG:PBD:PP= 50:10:10:30, Cured	1.44	2.65	7.59	10.2

7.3.3 Blends with Rubber: PP= 40: 60

Tensile Properties

Addition of curatives (DCP: S= 1: 1 at a total of 4% dosage) resulted in a little increase in EB only for two-component blends (Figure 7.22). Thus, it was found that the response of the blends towards addition of curatives decreases with an increase in PP amount. In fact, in the case of four-component blends (Figure 7.23), addition of curatives does not improve the properties at all. This supports the hypothesis that due to increased PP content, PBD and ENG were unable to compatibilize the PP and rubber phases.

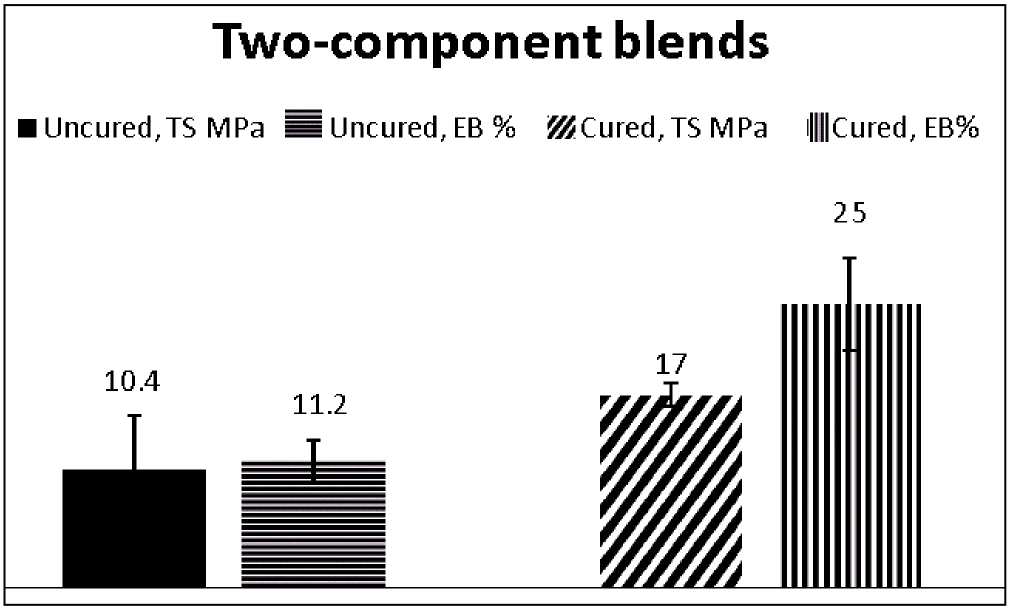


Figure 7.22 TS and EB of two-component blends, DRT: PP= 40: 60

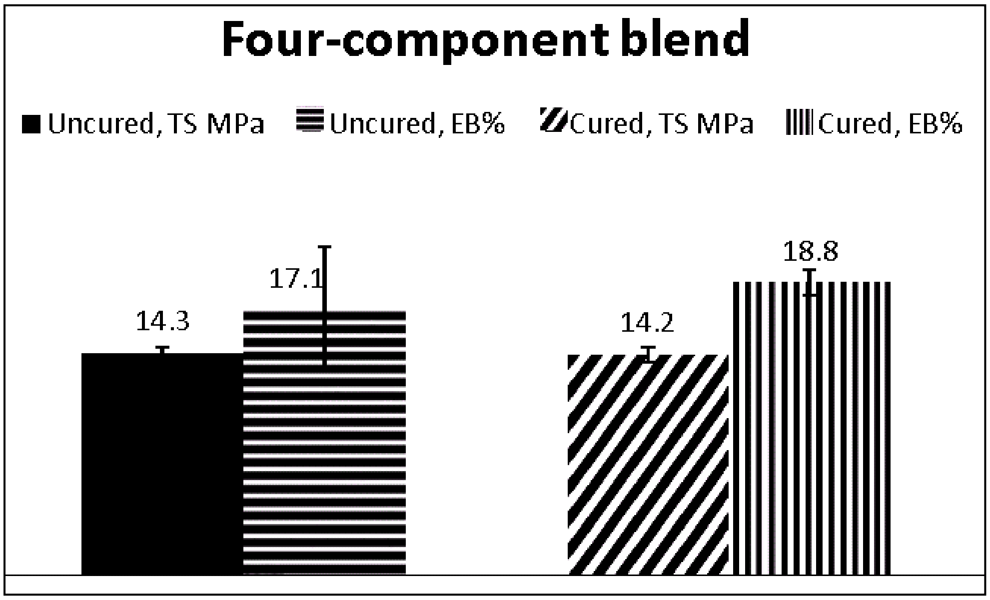
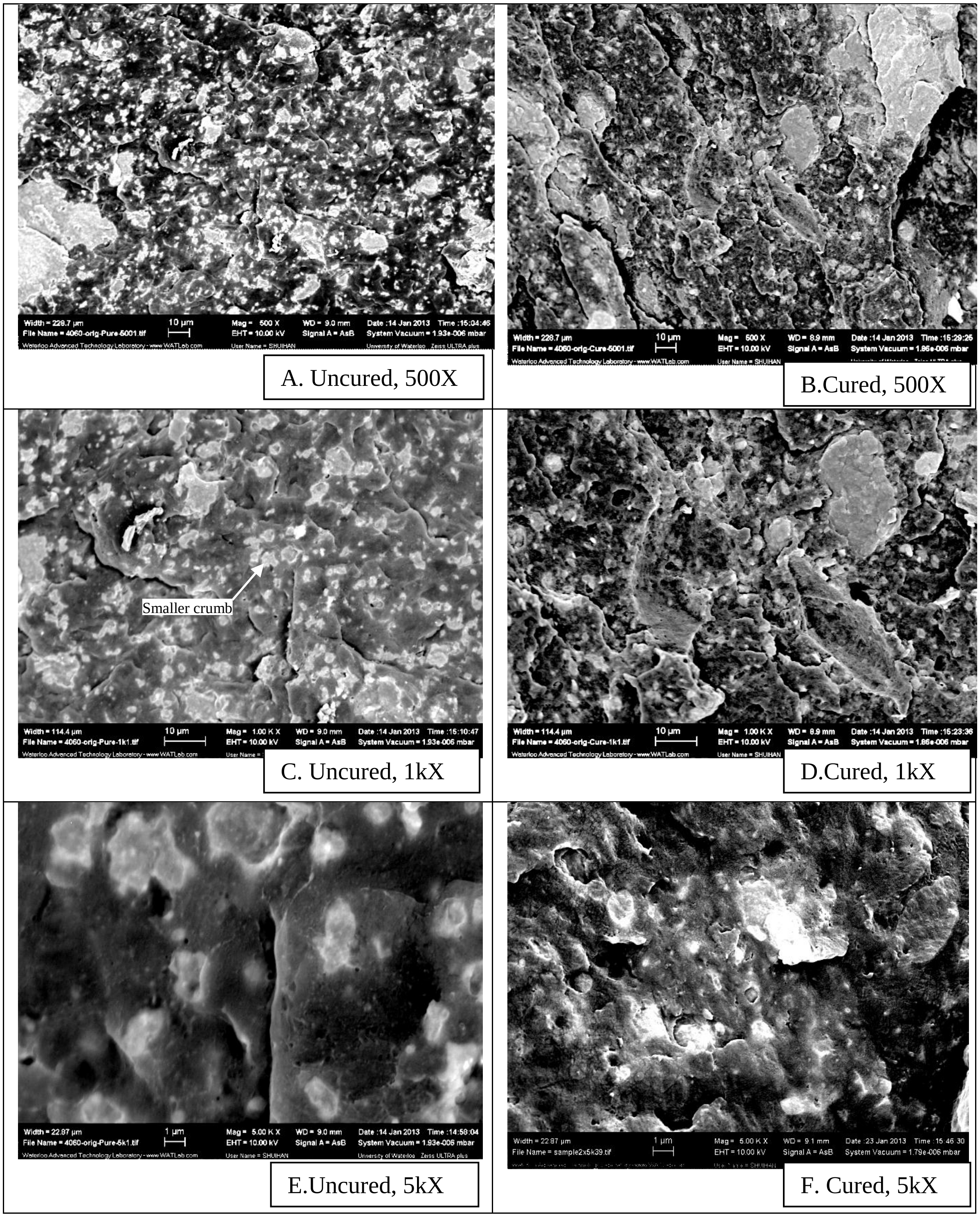


Figure 7.23 TS and EB of four-component blends, DRT: ENG: PBD: PP= 30: 10: 10: 50

Morphology

It was noticed in Figure 7.24 that addition of curing agents to two-component blend resulted in the formation of bigger rubber crumbs compared to the uncured blends. These crumbs were not darkened as in the case of earlier compositions. It was thought that this might be the reason for negligible improvement in properties in blends with higher plastic content. A similar observation was made for the four-component blend. As mentioned earlier, probably the amounts of PBD and ENG were insufficient for the blend, due to increased PP amounts. Due to this, the matrix phase, majorly consisting of PP phase, could not be compatibilized with DRT effectively. Also, in the cured four-component blends, the rubber crumbs appeared bigger than in the uncured blends (Figure 7.25), which is opposite to what is expected. The probable reason may be that upon addition of curatives (DCP and S), the plastic phase gets more densely crosslinked by sulphur bridges and therefore, the rubber domains were somehow forced to aggregate and increase in size. Crosslink density analysis confirmed that addition of curatives increased the crosslink density, which may have occurred predominantly in the PP phase, as there is no accompanying marked increase in EB. As crosslinks are not formed between the rubber crumbs and the matrix, no major improvement in properties are detected upon curing.



A. Uncured, 500X

B.Cured, 500X

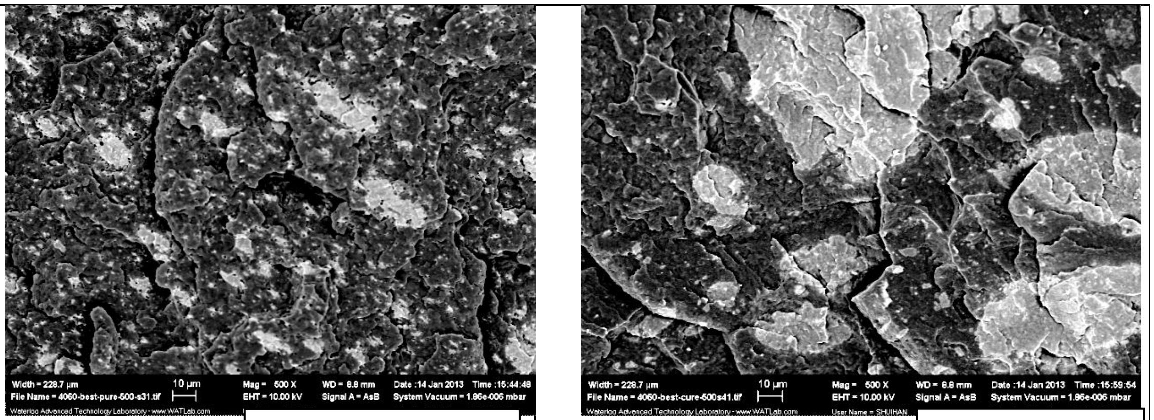
C. Uncured, 1kX

D.Cured, 1kX

E.Uncured, 5kX

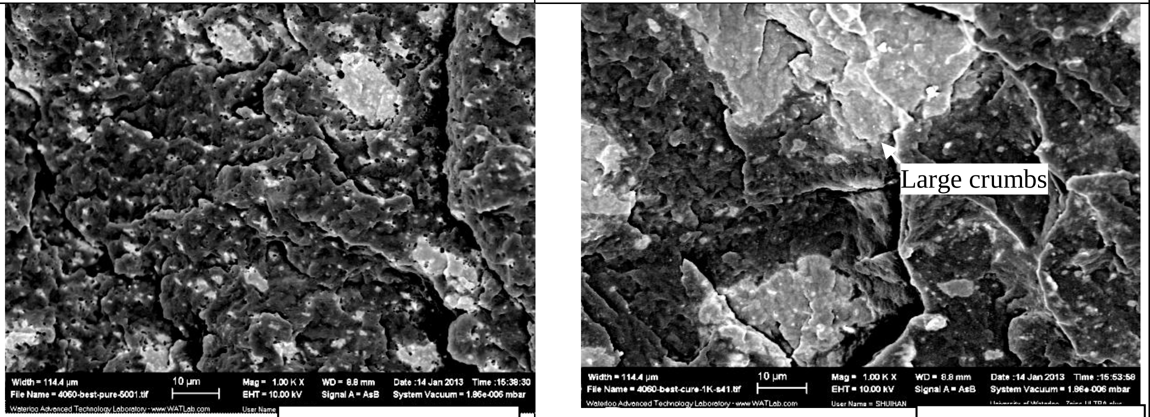
F. Cured, 5kX

Figure 7.24 SEM pictures for DRT: PP= 40: 60 blends



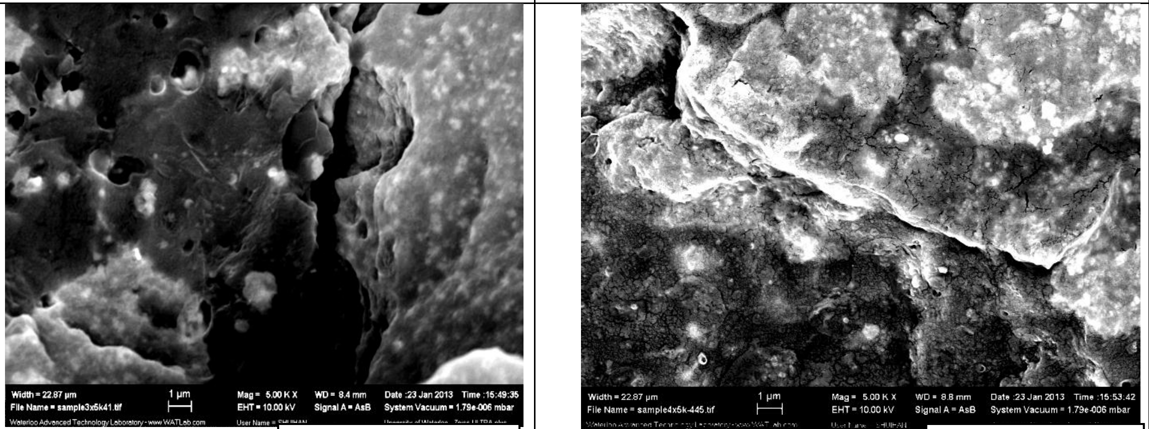
A. Uncured, 500X

B.Cured, 500X



C. Uncured, 1kX

D.Cured, 1kX



E.Uncured, 5kX

F.Cured, 5kX

Figure 7.25 SEM pictures for DRT: ENG: PBD: PP= 30: 10: 10: 50 blends

DSC

As observed previously, addition of curatives decreased degree of the crystallinity and melting point as compared to the uncured blends for all compositions (Table 7.8). The decrease in melting point is not as drastic as was in the case of the blends with 80% rubber, which showed a significant improvement in the properties upon addition of curatives.

Table 7.8 DSC results for TPOs/ TPVs having Rubber: PP= 40: 60

Composition	Melting point (°C)	Degree of crystallinity (%)
DRT:PP= 40:60, Uncured	167.6	37.0
DRT:PP= 40:60, Cured	163.8	29.0
DRT: ENG: PBD: PP= 30:10:10:50, Uncured	164.8	33.7
DRT: ENG: PBD: PP= 30:10:10:50, Cured	163.9	30.1

Soluble Content

Table 7.9 lists the percentage changes in weight after the samples were extracted by acetone, toluene and xylene one by one. Although, the properties of the four-component blend were not seen to increase upon curing, there is a decrease in sol content. This suggests that the crosslinking by the DCP/S system may have predominantly occurred in the PP phase. Thus, as the crosslinks did not occur between the phases, no major improvements in the properties were recorded.

Table 7.9 Soluble content for blends having Rubber: PP= 40: 60

Composition	Acetone extractable (AE) %	Toluene extractable (TE) %	Xylene extractable (XE) %	% Sol (TE + XE)
DRT:PP= 40:60, Uncured	0.36	3.82	22.61	26.4
DRT:PP= 40:60, Cured	1.25	1.54	9.97	11.5
DRT: ENG: PBD: PP= 30:10:10:50, Uncured	0.65	7.37	21.94	29.31
DRT: ENG: PBD: PP= 30:10:10:50, Cured	1.6	2.16	7.36	9.51

7.4 Potential for commercial applications

A comparison is made with a commercial TPV (Santoprene^{TM} 101-80) in Table 7.10 to investigate the value of DRT based TPVs. It can be seen that DRT based TPV displays similar properties as the commercial TPV except for EB and modulus values. Therefore, such a material can be used in those applications where the product is not subjected to high elongations. Santoprene^{TM} 101-80 is generally used in appliance components, automotive (underhood and bumpers) and consumer applications, electrical parts, gaskets, seals, tubing etc. Every application has its own requirements of mechanical properties, but the above listed applications are a good point to start exploring the use of DRT based TPVs.

Table 7.10 Comparison of properties of a commercial TPV with a DRT based TPV

	Santoprene^{TM} 101-80	**DRT: ENG: PBD: PP = 70:10:10:10**
TS (MPa)	11	10
Modulus @ 100%	4.7	7.9
EB (%)	540	150
Hardness (Shore A)	86	85
Compression Set (%)	41	40

7.5 Conclusions

Considering the results obtained, it seems reasonable to state that addition of maleic-anhydride grafted PP (Polybond®) and polyethylene-octene (Engage®) as compatibilizers along with curatives is beneficial to get good properties (especially at higher rubber dosages). PBD and ENG seem to act as binders for PP, as they have structural similarity to PP, and additionally PBD has double bonds to interact with rubber unsaturation.

Another finding was that the percentage improvement of properties in four-component blend upon addition of curatives, reduced with an increase in PP dosage (Figure 7.26). In fact, in blends with 60% PP there was almost no improvement in TS and only slight improvement in EB. It is proposed that this might be caused by an increase in the ratio of PP: PBD, which may have made it difficult for PBD to compatibilize PP and DRT.

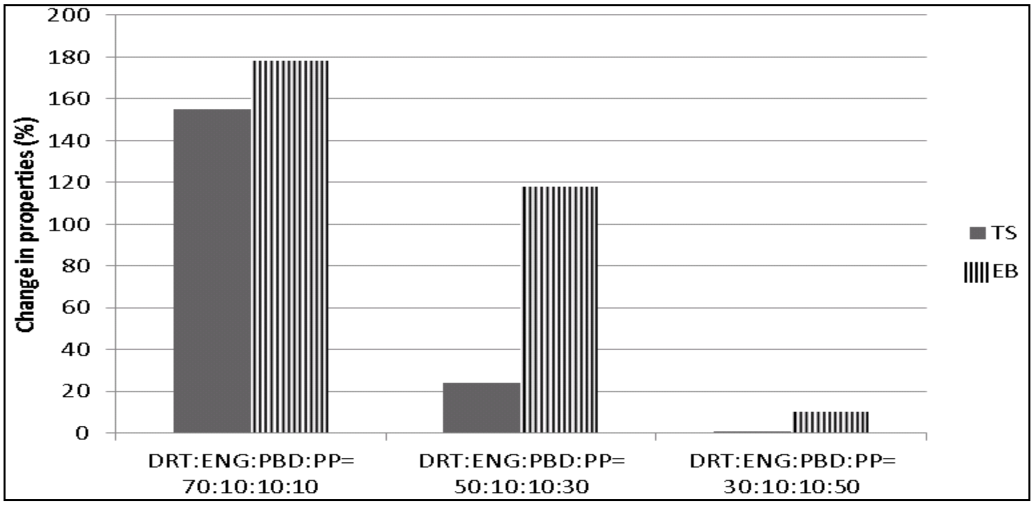


Figure 7.26 Percentage change in EB and TS upon curing with reference to uncured four-component blends

As the motive of the project was to prepare TPOs/ TPVs with higher ratio of DRT, further investigation at low DRT content is left for future work. On the whole, a unique complex combination of compatibilizers was discovered and successfully implemented on a TSE to prepare commercially useful TPVs based on DRT. Thus, the objectives of the work were successfully achieved.

CHAPTER 8

CONCLUDING REMARKS

8.1 Summary and Conclusions

This thesis has presented the work done with regard to preparation of TPVs using devulcanized rubber (DR) and polypropylene (PP). The objectives of the work were:

- To design a compatibilization system to blend DR and PP with an acceptable degree of compatibilization (indicated by at least 100% EB)
- To compare the performance of TPVs made from DR produced from tire rubber (DRT) and EPDM (DRE)
- To optimize the processing conditions in order to establish a continuous and stable extrusion process to produce DR based TPVs

Accordingly, the research optimized the compounding formulation and processing variables using DOEs and characterization techniques, in order to produce well compatibilized DRT based TPVs in a TSE.

Chapter 4 confirmed that DRT performs better than crumb rubber, and that there is a potential to explore the use of DRT in preparation of TPVs. Using mixture design approach and characterization techniques, DRT and PP matrix were proven to be mutually incompatible. Dynamic vulcanization (based on sulphur cure system) was shown to be ineffective in improving the properties. Model equations were developed to predict the TS and EB at given dosages of DRT, PP, sulphur and TBBS in the specific range, which was used for the experiments. The reluctance of rubber crumbs to interact with the matrix was detected as the prime reason for the poor properties of DRT / PP blends. Out of the various reactive and non-reactive compatibilizers tested, a combination of DCP and sulphur was found to significantly improve the properties by involving the crumbs to participate in reactions with the matrix.

Chapter 5 investigated the probable reactions that sulphur and DCP may be undergoing in DRT and PP blends. The study found that the probability of occurrences of various reactions depended on the composition of the system. It was proposed that sulphur had more affinity to react with tertiary radicals generated along the PP molecules than with peroxide radicals or unsaturation present in DRT. Therefore, a higher plastic to rubber ratio (having more tertiary PP molecules) favored the use of DCP and sulphur combination to get better properties; whereas, a higher rubber to plastic ratio required only DCP to get good properties. Sulphur proved to be a good coagent and effectively reduced the beta-scission degradation of the PP, along with forming sulphur bridges (when the PP content was higher). Model equations were developed to predict the TS and EB at any given amounts of DRT, PP, sulphur and DCP in the range, which was used for the experiments

Chapter 6 concluded that in TPVs based on DRE and PP, presence of sulphur was essential at all compositions for DCP to be an effective cure compatibilizer. EPDM was found to be prone to degradation by DCP indicating a behavior similar to EPR. As both EPDM and PP are susceptible to beta-scission degradation, use of a coagent was found to be mandatory. Thus, DRE behaved differently than DRT probably due to structural differences.

Sulphur, once again, proved to be a good coagent and effectively reduced the beta-scission degradation of PP and EPDM along with the formation of sulphur bridges. This resulted in a good morphology and better properties. Model equations were developed to predict the TS and EB at any given dosages of DRE, PP, sulphur and TBBS in the range, which was used for the experiments. Overall, DRE was found to be less responsive to curatives than DRT and performed relatively poorly.

In Chapter 7, addition of maleic-anhydride grafted PP (Polybond®) and polyethylene-octene copolymer (Engage®) as compatibilizers, along with DCP was discovered to be very beneficial to get good properties, especially at higher rubber dosages. Polybond® and Engage® seemed to act as binders for PP and DRT. The percentage improvement of properties upon addition of compatibilizers was found to reduce with an increase in PP amount. The reason for this was proposed to be the increase in the ratio of PP: PBD, which made it difficult for PBD to compatibilize the PP and DRT molecules.

On the whole, the novel contribution of this work to the field of engineering is the discovery of economically viable method to compatibilize DRT and PP. The properties obtained were in the range of 10 MPa (TS) and 180% (EB), with 85 Shore A hardness and 40% compression set. Such a material has a broad range of applications and can be easily tailor-made according to the requirements by varying the concentration of compatibilizers. Moreover, as the technology was successfully implemented on a TSE, achieving high throughputs of this material is easily achievable. The work has significantly boosted the possibility of commercializing DR based TPVs, which was the primary goal of the project.

8.2 Recommendations for Future Work

In the given timeframe of the project, not all the ideas generated could be explored. A few aspects of the research were found worth to be further investigated and developed. For instance, DRT in four-component blends can be replaced by DRE to evaluate the performance. Also, PP may be replaced with PE, and maleic anhydride functionalized PE can be used in place of maleic anhydride functionalized PP, to evaluate their influences on the properties. Engage® and Polybond® have a broad range of grades with different properties. These grades can be analyzed and used to tailor the properties for various applications. Other peroxides, such as Trigonox® 101, can be tested and the dosages of peroxide and sulphur could be varied across different ratios. This was found necessary especially in case of DRE (Chapter 6) based TPVs. Devulcanization and dynamic curing may be combined into a single step extrusion process, which would result in GTR as the feed material and TPVs as the end product. Solid state NMR may be used for characterization in order to get a better understanding of the molecular interactions.

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