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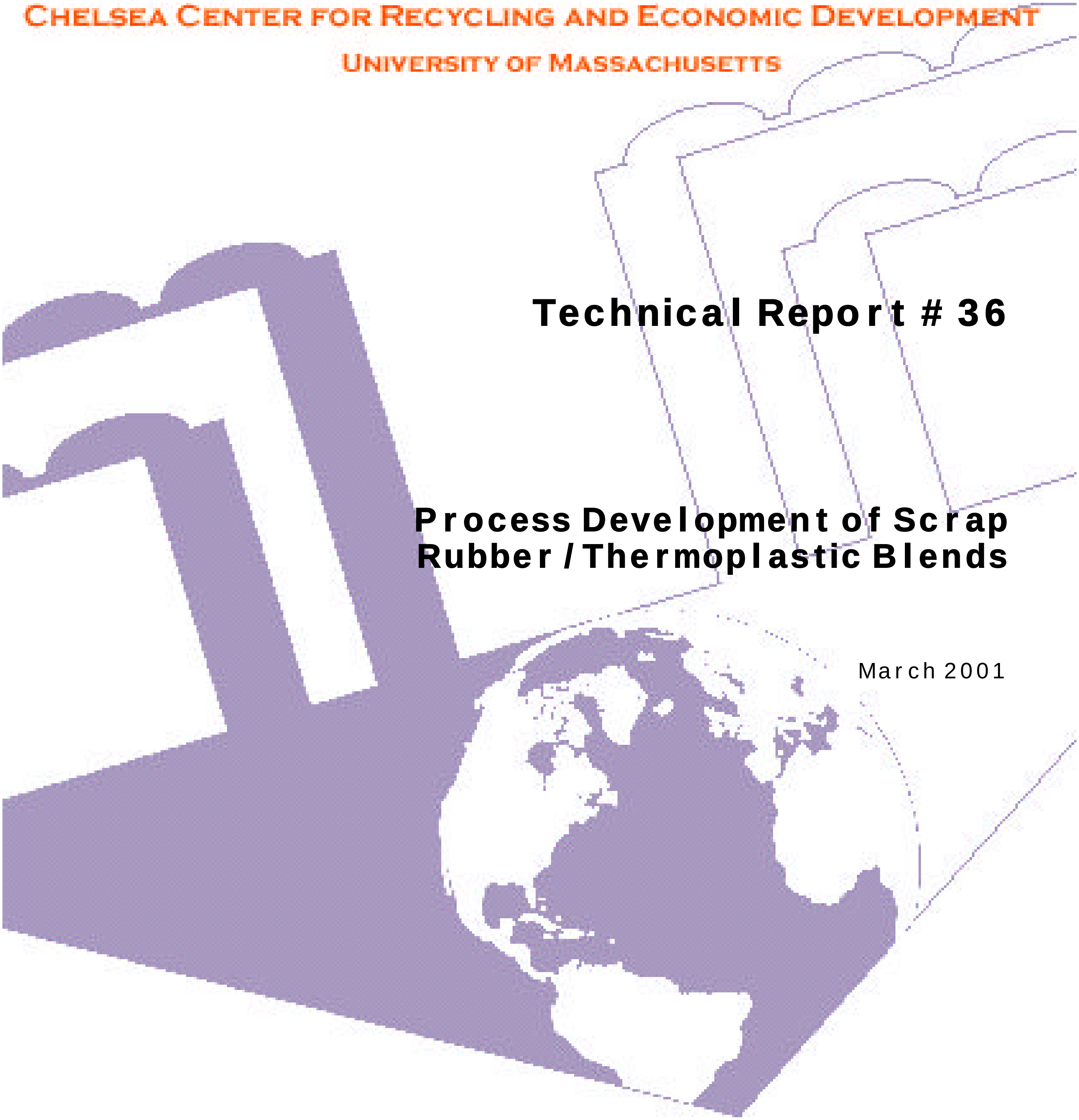

Technical Report # 36

Process Development of Scrap Rubber / Thermoplastic Blends

March 2001

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Process Development of Scrap Rubber / Thermoplastic Blends

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Chelsea Center for Recycling and Economic Development
Technical Research Program

March 2001

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1 INTRODUCTION

Scrap rubber recycling has become a statewide effort. It has been recognized that tire dumps/stockpiles introduced many environmental and health problems, as stated in "Waste Tire Recycling, Abatement, and Disposal Act of 1997" (Introduced in the Senate) [S 445 IS]:

1. The United States generates approximately 250,000,000 waste tires each year with over 3,000,000,000 waste tires stored or dumped in aboveground piles across the United States;
2. Current waste tire collection and disposal practices present a substantial threat to human health and environment;
3. Waste tire piles are a breeding opportunity habitat for disease-carrying mosquitoes, rodents and other pests and may be ignited causing potentially catastrophic fires.

Besides the public awareness, the reclaiming and recycling of tire rubber is also the subject of efforts from independent organizations and industries. The Scrap Tire Management Council (STMC), a subsidiary of the Rubber Manufacturers Association (RMA), started to organize industrial efforts and to promote the awareness of scrap tires as a valuable commodity. According to its study, only 22% of 200 million tires generated annually has been recycled in the forms of tire derived fuel (TDF), civil engineering applications, agricultural applications and etc. Among these reclaiming avenues, the majority of scrap tires were burnt for their high energy/mass ratio, despite the fact that it produces green house gas, fly ash, and toxic fumes on some occasions. Other applications use whole tire and crumbled rubber and are still in their primitive stage, where scrap rubber continues to pose a potential fire hazard.

The difficulty in rubber recycling lies in the fact that rubber is a thermoset material and attempts to recycle it in a manner similar to plastics often leads to structural breakdown and material decomposition. Automobile tires generally consist of 70wt% rubber and carbon black, and an estimated 2.4 million tons of scrap rubber are produced annually in the US. With the fast accumulation of scrap tires, increasing awareness of their potential hazard and continuous promotion of scrap rubber recycling from government, public and industries, new markets and new technologies must be created.

Incorporation of scrap rubber into thermoplastic elastomeric (TPE) materials is an appealing alternative to existing applications. Thermoplastic elastomers are a new family of materials, incorporating the advantages of both thermoplastics and elastomers. More importantly they are readily recyclable in a manners similar to thermoplastics. Applications for thermoplastic elastomers are expanding into many major areas, such as automobile parts, agricultural pipes, flooring and matting. Although the use of rubber in TPEs, especially virgin rubber, has been documented for years, the transformation of crosslinked rubber into a TPE remains a challenging problem, in spite of its attractive potential.

A simple approach to producing thermoplastic elastomers from recycled rubber is the compounding of ground scrap rubber into thermoplastics. Unfortunately, this approach has generated limited applicability due to the inadequate properties of the blends produced, even at low rubber content. The major reason is the difficulty in compatibilization of two different materials, particularly when one of the components is crosslinked. The quality of a blend is dependent on the degree of phase separation and the particle size of the dispersed phase. A high degree of incompatibility of the two materials results in large domains of the dispersed phase and poor mechanical properties. Compatibilization techniques are often used to improve the quality of the blend and increase the mechanical properties.

Studies of new thermoplastic elastomers developed from blends of ground scrap rubber with thermoplastics are presented in this report. Compatibilization techniques were employed to improve the mechanical properties of the resulting thermoplastic elastomers. The report is divided into four sections, which have been individually presented at national conferences. The first three sections deal with development of blends and compatibilization approaches. The last section is devoted to a scale-up study for processing the blends.

2 DEVELOPMENT OF NOVEL APPLICATIONS OF CROSSLINKED ELASTOMER SCRAP IN THERMOPLASTICS*

2.1 Abstract

Materials ranging from impact-modified thermoplastics to thermoplastic elastomers (TPE) can be obtained from blends of recycled ethylene-propylene-diene rubber (EPDM) containing carbon black with polypropylene (PP) by varying the ratio of components in the blend. This study focused on developing TPE materials from PP and recycled ground rubber. The effect of rubber particle size, melt flow index (MFI) for the PP, and weight percent of the constituent fractions on the physical properties of the resultant blends was quantified. A design of experiments based on the processing conditions and variables was performed to determine the optimum processing conditions.

Compatibilization techniques were used to improve the quality of the scrap rubber/plastic blends in response to the structural requirements of several potential applications. The cost factors for scale-up to manufacturing operations were also considered. It was found that the MFI of PP is a major factor controlling the mechanical properties of the blends. Through proper selection of the components and compatibilization techniques, blends were found to be tailorable to specific applications.

2.2 Introduction

During the past few years, there has been substantial progress in the recycling of polymeric materials. Particularly noteworthy has been the development of the Plastic Container Code System used by consumers and community groups to identify, separate, and recycle thermoplastic materials. Unfortunately, progress in the area of recycling thermosetting polymers, such as rubbers, has not been as successful, since these materials cannot be reformed once they have been crosslinked. As a result, other methods to recycle the rubber must be found. Grinding is one method to recycle a thermoset. The ground rubber can be used alone or mixed with thermoplastics to achieve the desired properties, such as impact modification.[1-4]

The market for thermoplastic elastomers has grown dramatically because of the ability to recycle and process these materials using conventional thermoplastics processing equipment.[5-8] The unique characteristics of thermoplastic elastomers make them an attractive alternative to conventional elastomers in a variety of markets, such as the automotive industry. Consequently, conversion of a conventional elastomer (thermoset) into a thermoplastic elastomer through blending with thermoplastics introduces new market applications for scrap rubber and many research efforts have been conducted in this area.[9-13]

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[*] H.S. Liu, C.P. Richard, J.L. Mead, and R.G. Stacer, "Development of Novel Applications of Crosslinked Elastomer Scrap in Thermoplastics", ANTEC 2000, 2884, (2000).

Pittolo and Burford[1] have studied the effect of scrap rubber in polystyrene (PS) to increase impact strength. Their preliminary investigations indicated that recycled rubber crumb acted as a toughening agent for the brittle thermoplastic. The toughness of the resultant materials increased with the degree of rubber/matrix adhesion and decreased with increasing rubber particle size. However, this limits the consumption of scrap rubber in such applications because no more than 20% of rubber is typically used in the blends. Other researchers[14] have studied blends of high-density polyethylene (HDPE) with recycled tire rubber. In this case, the authors found tensile strength and hardness decreased with greater rubber concentrations, and ductility improved above 5% rubber content. Data were reported only for rubber concentrations up to 30%. Chidambaram and Kim[15] studied the effect of surface treatment of rubber particles on reactive blending with polymethylmethacrylate and found that enhanced mechanical properties were possible.

In contrast to the aforementioned research, where limited amounts of rubber were consumed, this study focused on the development of thermoplastic elastomers by blending more than 50% of EPDM rubber into the composites. The resulting materials show excellent mechanical properties and may be suitable for a variety of applications.

2.3 Experimental Approach

2.3.1 Blending

Materials (EPDM rubber, 80 & 170 mesh, from Erickson Inc.; PP, 0.75 & 12 MFI, from Fina) were mixed in a Rheocord System 40 (Haake Buchler). After equilibrium temperature and screw speed were reached, the plastic material was added. The rubber portion was blended in after the plastic material was completely melted, as indicated by a stabilized torque reading, usually after 4 to 5 minutes. Mixing of the blend was stopped after a specified time (two to ten minutes), or when the torque became constant. The rubber-plastic composite was removed and then ground using a laboratory mill (Thomas Wiley, model 4) with a 40-mesh screen. If the particles were larger than 40 mesh, efficient compression molding proved to be difficult. Additional problems were caused by air gaps or voids between larger particle sizes. Deteriorated mechanical properties were among the directly observed results.

2.3.2 Molding

Compression molding was performed in a heated press (Carver, Model C). The machine was preheated to equilibrium at 225^{o}C. A square-shaped aluminum frame (90mm × 150mm) with a thickness of 1.5mm was sandwiched by two aluminum plates to form the mold. Rubber sheets were prepared using this process. During molding, materials were preheated for 5 minutes; then compressed to 30MPa for 5 minutes; pressure was then slowly ramped up to 100MPa during a 5-minute period. Sheets were cooled to room temperature under a 100MPa load using a Schrader cooling press. The sheets were then removed and die-cut into test specimens.

2.3.3 Testing

Tensile specimens were prepared using a ½ scale ASTM D412 die. Tensile testing was performed using an Instron 6025 with attached computer operating system and a crosshead speed of 5 cm/min. Elongation was determined using crosshead displacement and the gage section as the original length.

Shore A hardness tests were performed using a hand-held tester, following the procedures outlined in ASTM D2240. Ten readings across the length of the specimen were recorded for each sample.

Differential Scanning Calorimeter (DSC) characterization was performed using a TA Instruments' Module 912. Sample size ranged from 7.0 to 10.0mg, and a heating rate of 10°C/min was selected as a reference condition.

Dynamic Mechanical Analysis (DMA) was accomplished in forced dynamic shear using a rectangular torsion specimen in a Rheometrics 605. Temperature sweeps were performed over the range from –100°C to 50°C with heating rate of 3°C/min.

2.4 Results

A major challenge to blending recycled EPDM with PP is the incompatibility between the two materials. PP is a semi-crystalline material while EDPM is an amorphous thermoset. Crystalline segments within the PP are resistant to intrusion of EPDM segments. Crosslinking of the EPDM makes it difficult for PP to disperse during mixing. Therefore, compatiblizing techniques were generally required to obtain the desired physical properties.

2.4.1 Compatibilizing Techniques

Since the majority of the double bonds in the recycled EPDM are still available even though it is vulcanized, by adding appropriate grafting agents, those double bonds can be utilized to graft PP onto the rubber particle surface. This reaction leads to better compatibilization between the PP and EPDM phases. Additionally, the reactive blending with high rubber content may also promote crosslinking between rubber particles. Figure 1 shows the two possible reactions during reactive blending. Considering the processing temperature (~200°C), t-butyl hydroperoxide with a half-life of 4.81 hrs at 175°C, was chosen for the reactive blending.

Figure 2 presents the tensile strengths of the EPDM/PP blends both with and without reactive processing. Two observations are readily apparent. First, the stress capability of the blend decreases as the rubber content goes up. Basically, this can be explained through a volume rule of additivity where the higher strength PP molecules are gradually replaced by the lower strength EPDM phase. Secondly, reactive blending dramatically enhanced the stress capability of all the blends. Percentage increases as great as 80% at the highest rubber content were observed.

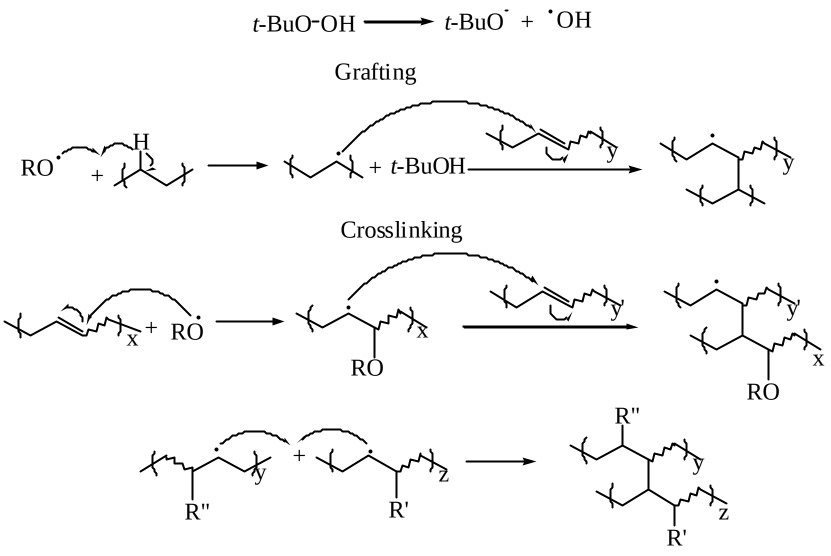

Figure 1. Postulated reactions during reactive blending.

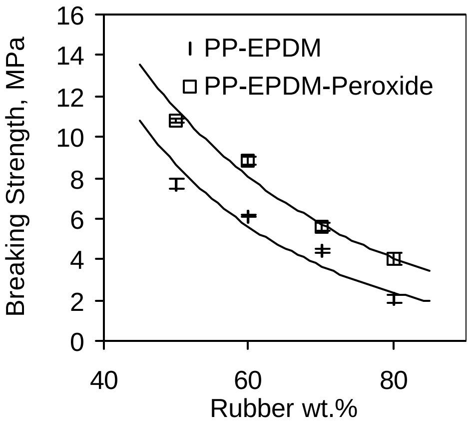

Figure 2. Break tensile strength of recycled EPDM/PP blends.

Figure 3 shows the elongational capability results that correspond to the breaking stresses reported in Figure 2. Reactive blending again provided significant improvement in all cases. Samples without reactive blending did not even provide rubberlike properties. Specifically, elongational capabilities of the reactive blends of 105% and 110% were obtained at 50 and 80% rubber content, respectively.

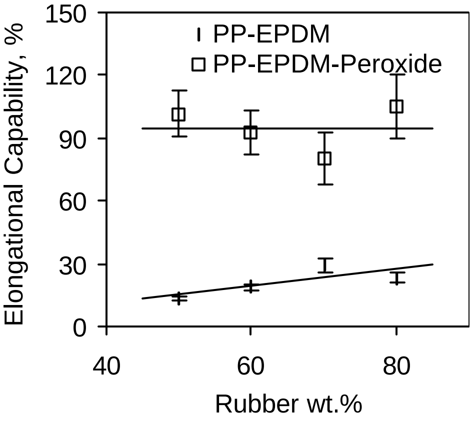

Figure 3. Break elongation of recycled EPDM/PP blends.

A plausible explanation for the above results is a change in crystallinity. As shown in Figure 4, as the rubber wt.% increases, PP crystallinity decreases. This suggests that superior dispersion of PP in the rubber matrix was obtained. Also Figure 4 indicates that the addition of the peroxide initiates certain reactions, which in turn reduce the degree of crystallinity. This results in higher compatibility of the plastic phase within the rubber phase. Better reaction leads to superior tensile properties.

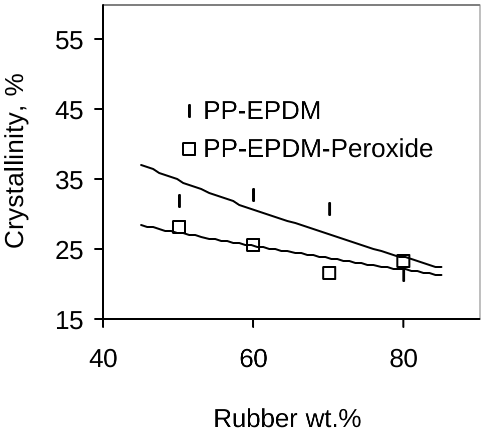

Figure 4. Crystallinity of recycled EPDM/PP blends.

Evidence that both materials continue to exist as separate phases within the blend can be seen in Figure 5. This figure presents DMA results for the 50/50 wt.% blend. Two dispersion peaks are clearly apparent in both the G" (shear loss modulus) and tan δ data. The low temperature dispersion peak for G" occurs at -60^{o}C, closely approximating the glass transition temperature (T_g) of the pure EPDM. Similarly, the other peak in G" occurs near -2^{o}C, or the T_g of the PP.

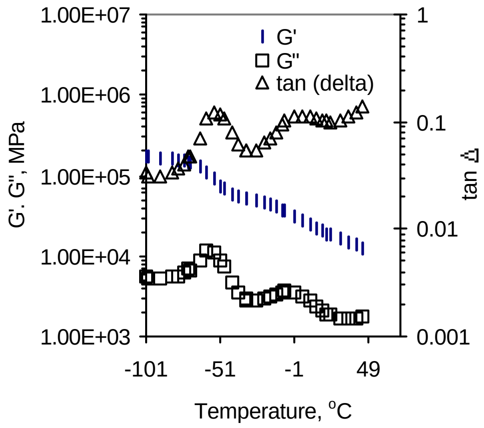

Figure 5. Dynamic mechanical analysis of EPDM/PP blend (50/50 weight %).

2.4.2 Identification of Optimum Blending Conditions

In addition to material factors, processing conditions can also affect the properties of the blends. In order to determine the optimum blending conditions, a design of experiments (DOE) on the processing conditions and other variables was performed. Six factors with two levels were investigated in EPDM/PP blending. These factors and the experimental parameters investigated are shown in Table 1.

DOE results indicated that none of the factors in Table 1 or the interaction between these factors had an appreciable influence on the breaking strength of the blends. On the other hand, elongational capability results identified the MFI of the PP as a critical factor. That is, the higher the melt flow for the PP, the lower the elongational capability. This is somewhat counter-intuitive since a high MFI indicates lower molecular weight, which suggests better mixing or blending. An explanation for this unexpected behavior can be obtained from the crystallinity change of the PP. The lower the melt flow of PP, the higher the molecular weight and the lower the crystallinity. Additional discussion of this phenomenon will be given later after the results from the MFI blending have been presented.

Table 1. Controlled Factors and Levels in Experimental Design.

Factors	Low	High
Blending Temperature	190°C	220°C
Blending Speed	30 rpm	60 rpm
Blending Time	2 mins	6 mins
wt.% of Peroxide with Respect to Rubber	0.5%	1%
Rubber Particle Size	80 mesh	170 mesh
MFI of PP	0.45 g/10min	12 g/10min

A second important factor identified from the DOE is the size of the rubber particles. Specifically, the smaller the rubber particle, the greater the elongational capability. This is believed to be related to the larger rubber surface area of the small rubber particle system, which provides better compatibility, and, hence, enhanced elongational capability. The effect of particle size on mechanical properties has been also observed in the work of Coran and Patel.[16]

2.4.3 Influence of MFI of PP

As previously discussed, the two most significant factors establishing the mechanical properties of the blends are the MFI of PP and the rubber particle size. Hence, additional investigations were conducted on the influence of MFI by preparing blends using different MFI of PP and EPDM rubber. For this limited portion of the study, reactive blending was not utilized.

Two PP with different MFI values (12 and 0.75) were blended with the recycled EPDM. Resultant stress capability data are presented in Figure 6. As before, breaking stress decreases as the rubber content increases. Effect of the lower MFI can be seen as an approximately 5 MPa increase in stress capability for all blends considered. Even greater improvements were observed when elongational capability was considered. These data are presented in Figure 7. By changing the MFI of the PP from 12 to 0.75 MFI, a doubling in the strain capability was observed. The relationship between these results and the crystallinity of the PP phase can be seen through Figure 8. This figure shows that lower MFI PP has less crystallinity, which suggests better compatibility between the two phases.

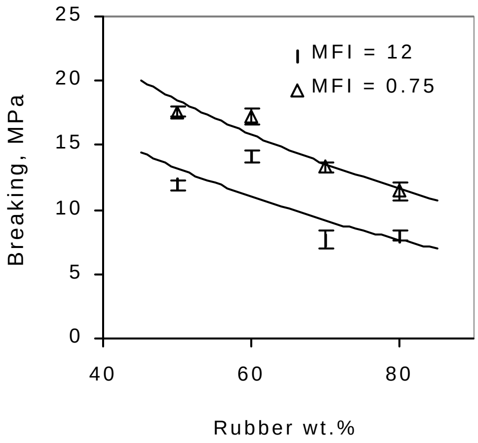

Figure 6. Influence of MFI of PP on break tensile strength.

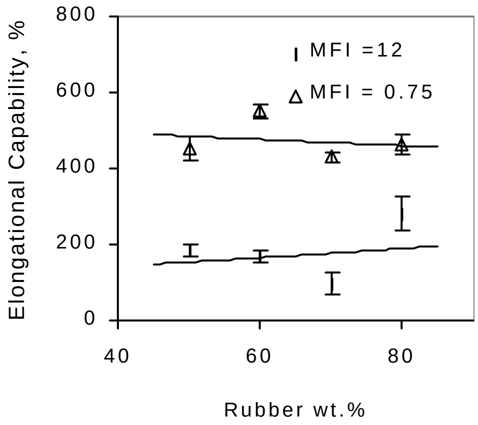

Figure 7. Influence of MFI of PP on break elongation.

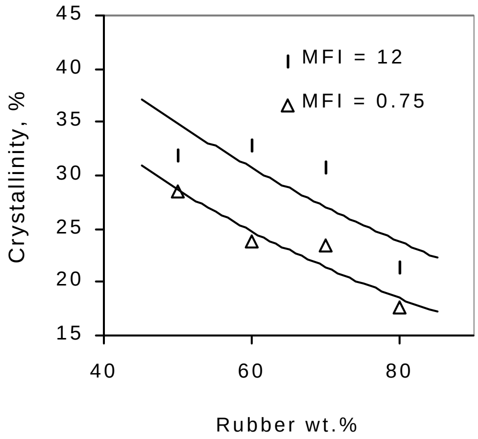

Figure 8. Influence of MFI of PP on degree of crystallinity.

2.4.4 Summary

A system diagram, Figure 9, was constructed to summarize the above findings. It is concluded over a very broad range that the mechanical properties, as evidenced by stress and strain capability, of blends from PP and recycled EPDM rubber can be tailored by varying ingredients, MFI of PP, weight percentage of recycled rubber, and/or adapting different compatiblizing techniques.[17]

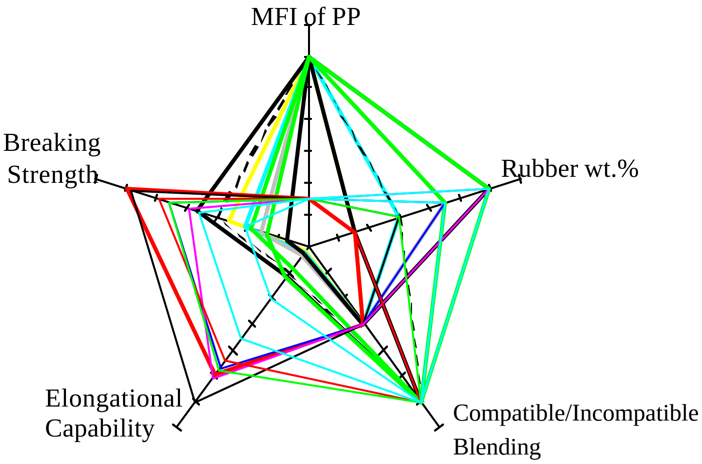

Figure 9. Thermoplastic elastomer from recycled rubber and plastics.

2.4.5 Market Analysis

Among the many possible applications for recycled rubber and PP blends, two readily feasible applications are roofing and flooring. These two applications were chosen for consideration because the physical properties of the blends are comparable to that of current commercial products.

Price comparisons were performed for the construction of a basketball court, a tennis court and a roller hockey rink. These are shown in Table 2. The cost comparison takes into account the percentage of rubber or PP used in the experimental blend, the exponential factor for a scale-up process and the overall surface area of the specific application. As shown in the table, material cost reductions of between 30 and 50% are possible from the experimental blends presented in this paper.

Table 2. Price Comparison of Commercial Products and Experimental Blends

EPDM/PP Ratio	Experimental. Blends	Commercial Product
	Basketball Court Price	
80/20	$6,902	$13,104
70/30	$7,888	$13,104
60/40	$7,888	$13,104
	Tennis Court Price	
80/20	$12,517	$22,512
70/30	$14,305	$22,512
60/40	$14,305	$22,512
	Roller Hockey Court Price	
80/20	$38,484	$62,496
70/30	$43,982	$62,496
60/40	$43,982	$62,496

2.5 Conclusions

This work has evaluated methods of using recycled scrap rubber in the development of new materials on a laboratory scale. Specifically, the recycled ground rubber was blended with PP to form a thermoplastic elastomer appropriate for use in sports surfaces, flooring, roofing, automobile trunk and window seals, etc. In addition, this work has converted a thermoset material into a thermoplastic elastomer, which can be reused and converted into new products.

The investigation of the rubber particle size, MFI of the PP, and weight percent rubber on the physical properties of the blends has been performed, in addition to the development of the compatibilization techniques. It is concluded that MFI of the PP and the rubber particle size are key factors to the mechanical properties of the blends. Results of this work can be used to guide manufacturers in developing recycled rubber/plastic blends with superior properties.

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3 THERMOPLASTIC ELASTOMERS AND RUBBER-TOUGHENED PLASTICS FROM RECYCLED RUBBER AND PLASTICS*

3.1 Abstract

An experimental investigation has been conducted to evaluate the use of recycled rubbers in blends for the development of new thermoplastic elastomers (TPE) and rubber-toughened plastics. The 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 Buechler batch mixer over a broad range of constituent fractions. Compatibilization and reactive blending techniques were used to improve the quality of the scrap rubber/plastic blends with respect to both mechanical and rheological properties. Results indicate that these blending techniques are 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 later conclusion was attributed to a lower degree of crystallinity in the PP phase that contributes to better blending between the phases.

3.2 Introduction

Blending recycled rubber with other materials has been an attractive alternate to disposal methods for many years. Its chief drawback has been the difficulties in obtaining adequate properties from the resultant blends. Efforts to develop recycled rubber/plastic blends have logically followed earlier blending research that produced both thermoplastic elastomers[1] and rubber-toughened plastics[2]. Results of these numerous studies on virgin materials have provided criteria for a successful blend. First, the two components must be thermodynamically incompatible enough to phase separate but not so dissimilar that intimate intermixing cannot be accomplished[1,3-7]. This criterion implies that the domain size of the dispersed phase must be small so that interfacial surface area is maximized, and leads to limits on the mismatch between the solubility parameters of the two components[1,3,5,7]. Secondly, crosslinking of the rubber phase through processes such as "dynamic vulcanization" is required to reduce creep in TPEs and enhance the strength of toughened plastics[1,8-9]. Finally, compatibilizers that act as interphase bridges between hard and soft phases are often required[10-15]. Of the various blends that have been reduced to practice, those based on the EPDM/polypropylene combination have been by far the most successful[1,9,16].

Extension of these blending technologies to their utilization of recycled rubber has progressed more slowly. Early investigators focused on both rubber particle size

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[*] H.S. Liu, J.L. Mead, and R.G. Stacer, "Thermoplastic Elastomers and Rubber-Toughened Plastics from Recycled Rubber and Plastics", presented at a meeting of the Rubber Division, American Chemical Society, Dallas, Texas, April 2000

reduction and surface reactivity of the resultant particle as a function of size reduction methodology[17-21]. These results are consistent with the aforementioned domain size arguments forwarded for TPEs and toughened plastics. Subsequent research indicated that inclusion of recycled rubber directly into either virgin rubber or plastics results in a degradation of mechanical properties[18-19,22-24]. As an approach to overcoming this problem, researchers incorporated a number of different compatibilizers and modification techniques[18-19,24-29]. Scale-up problems arose from changes in residence-time distributions, however, in transitioning from laboratory batch mixers to larger, continuous processing equipment[29]. Further complicating the issue is the wide variety of recycled rubber compounds and, in many cases, their inherent commingled nature. Consequently, it is often necessary to modify the blending operation for each specific recycled rubber received.

The objective of this research effort was to develop and demonstrate an approach for producing novel TPEs and toughened plastics from a range of recycled rubbers blended with PP. Attempts are made, where possible, to quantify important molecular structure/physical properties relationships in the various blends, as well as critical rheological and processing parameters. Reactive processing is used in the final product in all cases. Details on the compatibilizers used are given along with postulated mechanisms for their performance. Finally, scale-up from a Haake Buechler batch mixer to twin-screw extrusion is reported.

3.3 Experimental

3.3.1 Materials

Table 3 presents characterization data for the five recycled rubber compounds considered. They comprise three EPDM compounds, one SBR compound, and an NR/SBR blend. The EPDM materials were from recycled shoe sole and roofing applications as indicated, while the SBR and NR/SBR materials originated from scrap automotive tires. All five were obtained from the indicated commercial sources. Particle size reduction was accomplished by the commercial sources using ambient temperature underwater processing. Reported particle sizes were converted from the mesh sizes provided by the processors. Densities were also provided by the suppliers. The glass transition temperature T_g data were obtained from mechanical testing as detailed later.

Table 3. Recycled Rubber Characterization Data

Material	Supplier	Source	Particle Size (μm)	ρ (g/cc)	T_g (^{o}C)
EPDM-1	Erickson	Shoe Sole	177	1.19	-55
EPDM-2	Rouse	Roofing	89	1.14	-
EPDM-3	Rouse	Roofing	177	1.14	-
SBR	Erickson	Tire	89	-	-56
NR/SBR	Rouse	Tire	89	1.14	-

Table 4 lists the five polypropylenes investigated as part of this study. They represent a series of different of molecular weights, as well as including samples from two different sources. A broad range of molecular weights was selected to expand upon an earlier study[24] that suggested the melt-flow index of the PP played a critical role in the properties of EPDM/PP blends. Molecular weight data were provided by the manufacturers, while all the other characterization data were measured as described later.

Table 4. Characterization Data For Polypropylenes

Material	Supplier	M_n (D)	M_w/M_n	T_m (^oC)	Crystallinity (%)	σ_b (Mpa)	σ_y (MPa)	ε_b (%)
PP-3181	Fina	84	6.1	172	30	41	30	760
PP-3429	Fina	40	7.0	171	42	44	32	844
PP-3622	Fina	29	6.6	173	55	28	32	672
PP-3761	Fina	27	7.4	171	59	16	32	528
PP-4011	Huntsman				65	17	37	512

Chemical additives used in this study were t-butyl hydroperoxide from Aldrich Chemical Co. and SP-1045 (heat reactive octylphenol-formaldehyde resin which contains methylol groups) from Schenectady International Inc. *t*-Butyl hydroperoxide was chosen based on its half life of initiation at processing temperature, 200^{o}C, and used as radical initiator during reactive EPDM/PP blending. The SP-1045 material was used in SBR/PP blends.

3.3.2 Blending

Batch mixing was performed in a torque rheometer (Haake Buechler Rheocord System 40). The mixer was preheated to the mixing temperature, 200^{o}C, until stable. This usually took approximately 30 to 45 minutes. The rotor speed was set at 30 rpm. The rubber component was added when the PP was completely melted as indicated by a stabilized torque reading. In the case of EPDM/PP reactive blending, chemical additives were added two minutes after the addition of the rubber. Mixing continued for an additional two minutes. For SBR/PP and NR/SBR/PP blending, the previously reported processing conditions of Coran and Patel[30] were followed.

3.3.3 Specimen Molding

Compression molding was performed using a heated press (Carver, Model C) from a sandwich mold with a middle frame made from a 2 mm thick aluminum sheet. Rubber/plastic blends prepared by batch processing were placed between the platens, which were preheated to 225^{o}C. The blend was preheated for two minutes and then gradually compressed to a piston pressure of 30 MPa for an additional three minutes. Molded sheets were cooled to room temperature under a piston pressure of 100 MPa using a Schrader cooling press. The sheet was then removed and die-cut for the appropriate tests.

3.3.4 Characterization and Properties Testing

Differential scanning calorimeter (DSC) characterization was carried out using a TA Instruments' Module 912. Sample size ranged from 7.0 to 10.0 mg, and a heating rate of 10^{o}C/min was selected. Thermodynamic melting temperatures Tm were measured from the peaks in the heat flow curves. Percent crystallinity W_c was calculated from

$$W_c = \frac{\Delta H_f}{(\Delta H_f)_c} \tag{1}$$

where ΔHf is the enthalpy of fusion obtained from integration of the melt curve and (ΔH_f)c represents the corresponding literature[31] value for the pure crystalline material.

Dynamic mechanical analysis (DMA) was accomplished in forced dynamic shear using a rectangular torsion specimen in a Rheometrics 605. Specimens were sheared at a frequency of 1 Hz and an amplitude of 0.2 percent. Temperature sweeps were performed over the range from –100 to 50^{o}C with heating rate of 3^{o}C/min. Reported T_g values were obtained from dispersion peaks in the shear loss modulus G" curves.

Apparent viscosities η were measured with a capillary rheometer (Kayeness, Galaxy IV) at 200^{o}C. A die with an L/D ratio of 10/1 was used in all cases. Each flow curve was generated from data collected at nine different shear rates ranging from 10 to 5000 s^{-1}. Data were reduced using a two-parameter power law equation

$$\eta = k \left| \frac{\dot{\gamma}}{\dot{\gamma}_o} \right|^{n-1} \tag{2}$$

where k is the consistency index, n is the power law exponent, and $\dot{\gamma}$ and $\dot{\gamma}_o$ represent the shear rate and a reference shear rate of 1 s^{-1}, respectively.

Tensile specimens from compression molded sheets were prepared using a half scale ASTM D638 die D. Tensile testing was performed on an Instron 6025 with attached computer operating system and a crosshead speed of 50 mm/min. Strain was determined from the change in effective gauge length by optical methods.

3.4 Results and Discussion

3.4.1 Rheological Data for Simple Blends

Dynamic mechanical properties data in the form of temperature sweeps for four simple blends are collected in Figure 10. By simple blends, we refer to a blend in which reactive blending was not accomplished. Properties presented in these curves are shear storage modulus G', shear loss modulus G", and their ratio tan δ = G"/G'. Recycled EPDM-1 and SBR blended with a high-flow polypropylene (PP-3761) at two rubber weight fractions of 50 and 80 percent are shown in this figure. These were the only four blends characterized in this manner.

Evidence of phase separation behavior can be seen in all cases as high and low temperature dispersion peaks in both the G" and tan δ curves. Phase separation is a required criterion in the basic theories[1,2,9] for how these blends function. The low temperature peaks center at –55 and –56 ^{o}C for the EPDM and SBR blends, respectively. These are consistent with the glass transition temperatures of the soft phases. The corresponding high temperature peak is just below 0^{o}C, which is near the T_g of the PP. All four G’ curves reach a glassy plateau at approximately 2 GPa, which appears to be independent of rubber content. As temperature increases, however, G’ enters the transition region, which is more distinct for the blends containing 80 percent rubber. At the highest temperatures, G’ reaches a rubbery plateau of approximately 100 MPa for the blends with 50 percent rubber and 10 MPa for the higher rubber content blends.

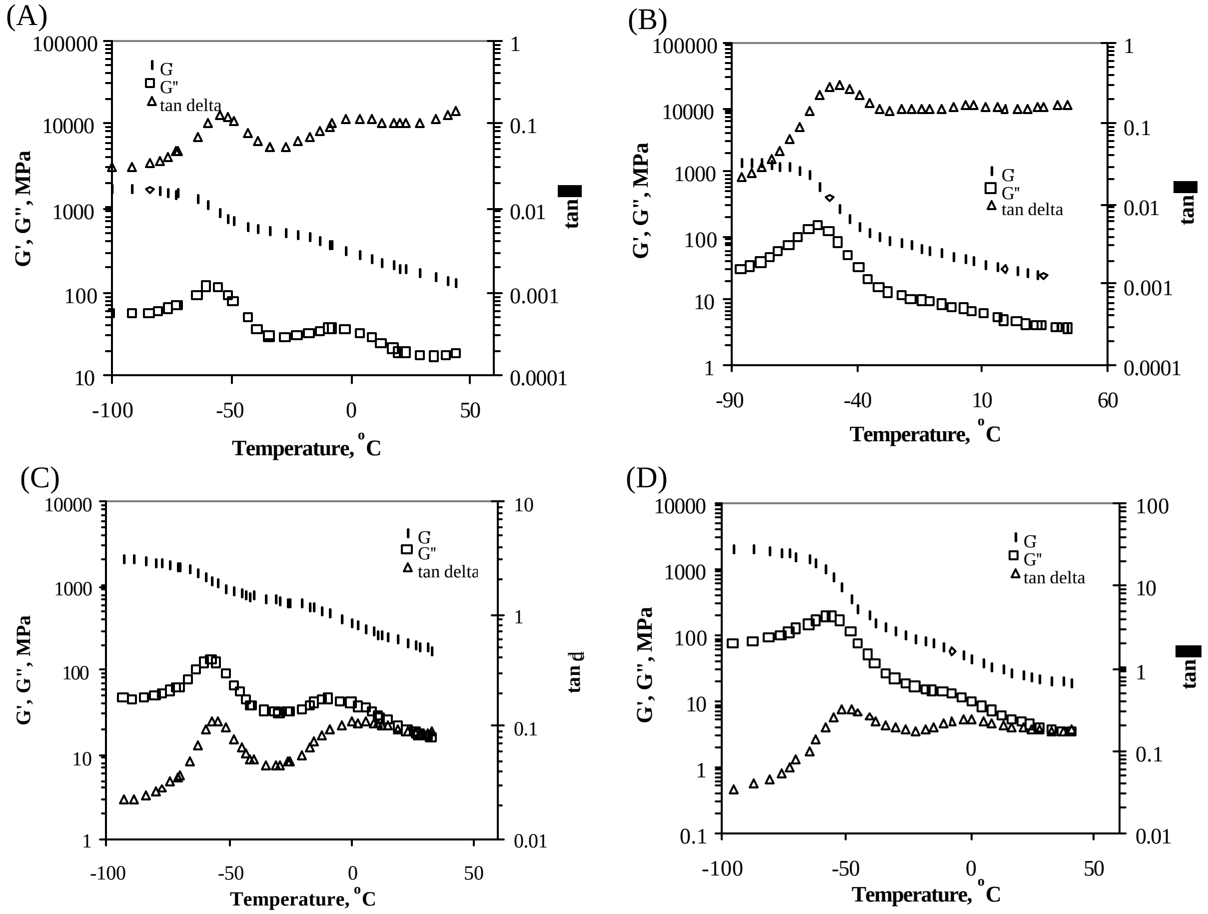


Figure 10. Dynamic properties data for rubber/plastics blends as indicated: (A) 50% EPDM-1/PP-3761, (B) 80% EPDM-1/PP-3761, (C) 50% SBR/PP-3761, and (D) 80% SBR/PP-3761.

Flow curves for 10 simple rubber/plastic blends were generated using capillary rheometry as discussed earlier. Rubber weight content was varied from 10 to 80 percent for each rubber/plastic blend. Figure 11 presents representative flow curves for the EPDM-1/PP-3761 blend at eight different rubber concentrations. Strong pseudoplastic behavior is observed in all cases. Similar data were collected for all 72 rubber/plastic blends considered. Data were reduced using Equation (2). Resultant power law exponents n and consistency indices *k* are tabulated in Table 5. They are also plotted as functions of rubber content in Figure 12 to illustrate distinct behaviors within the EPDM blends [Figures 12(A) and 12(B)], effect of EPDM particle size [Figures 12(C) and 12(D)], and differences within the SBR blends [Figures 12(E) and 12(F)].

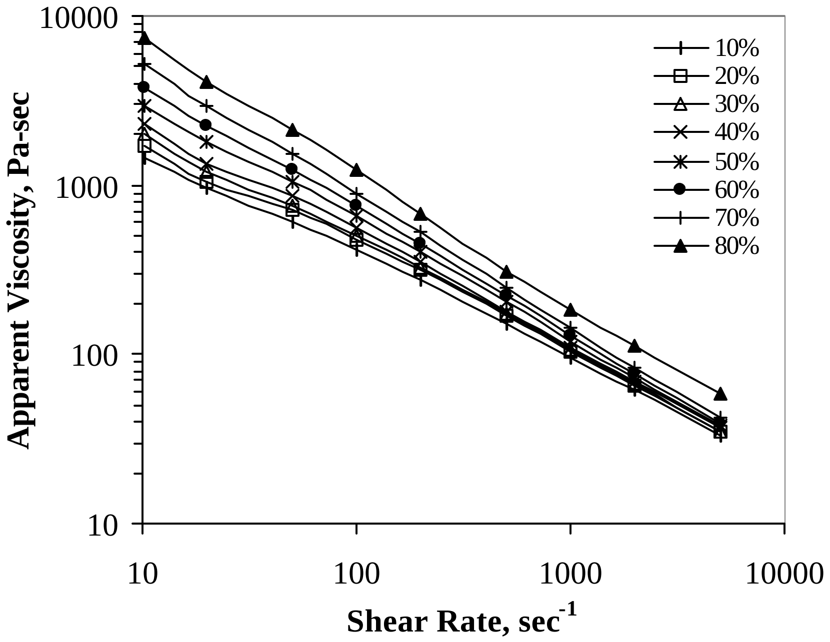


Figure 11. Representative flow curves for EPDM-1/PP-3761 for the eight rubber fractions indicated.

In general, n decreases while *k* increases as more rubber is added to the blend. The increase in *k* with crosslinked rubber content is consistent with the general theory for the rheology of suspensions, where resistance to flow of a composite increases exponentially with content of the dispersed phase. In this case, the carbon black filled, crosslinked elastomer acted as the dispersed solid while the PP melt served as the continuous phase. Nielsen and Landel[32] point out that hundreds of equations have been proposed to model this type of behavior dependent on the nature of the interaction between the two phases. For these blends, the viscosity rise is not as pronounced as would be expected from a rigid, solid filler, a feature that is believed attributable to the deformable nature of the rubber particles.

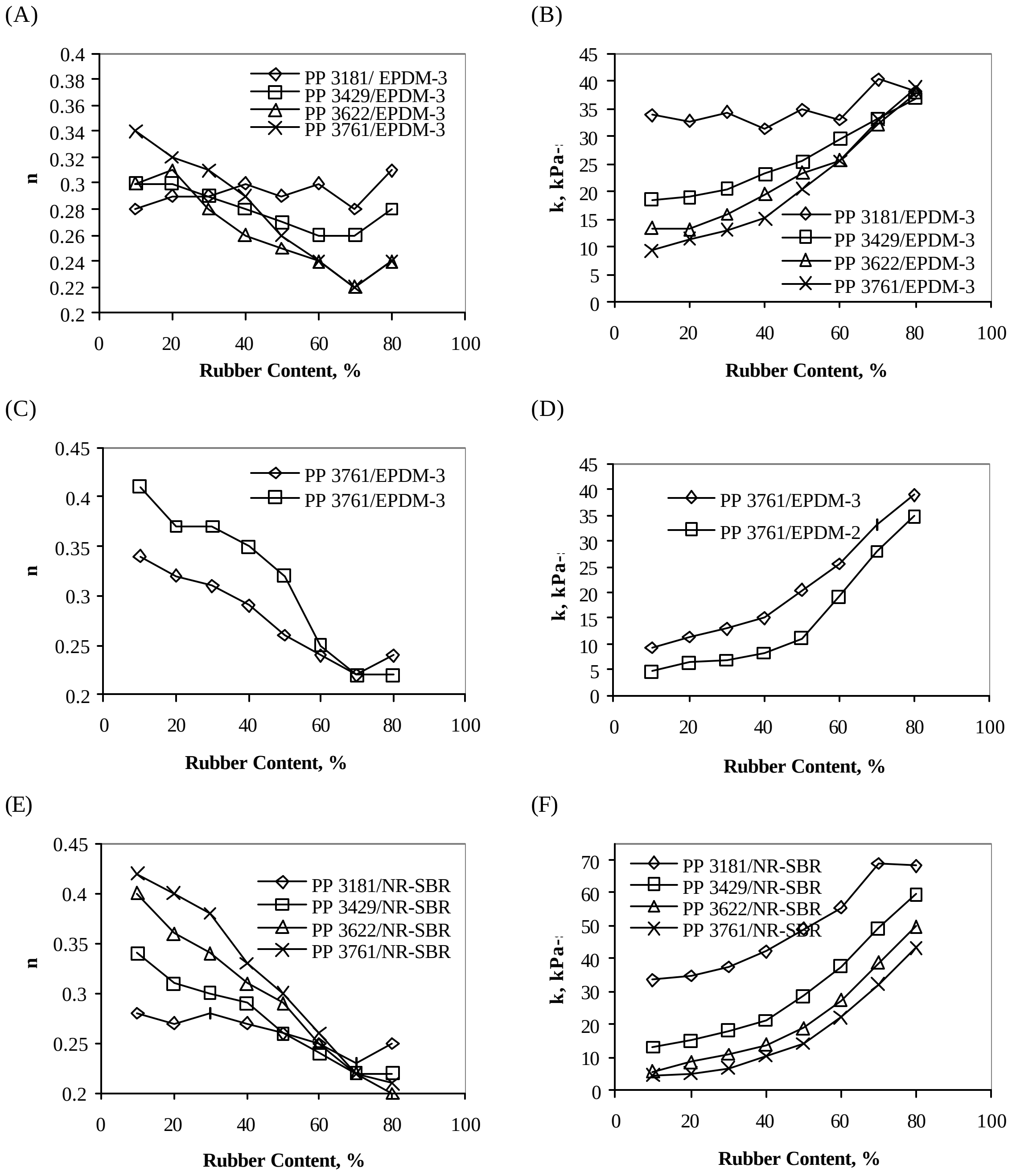


Figure 12. Reduced power law exponents and consistency indices as functions of rubber fraction for 10 simple blends as indicated.

Table 5. Power-Law Exponents and Consistency Indices of Recycled Rubber-PP Blends

PP	Rubber		Rubber Content, %							
			10	20	30	40	50	60	70	80
3181	EPDM-3	n	0.28	0.29	0.29	0.30	0.29	0.30	0.28	0.31
		k (kPa-sec)	33.78	32.68	34.35	31.41	34.76	32.99	40.27	38.17
3429	EPDM-3	n	0.30	0.30	0.29	0.28	0.27	0.26	0.26	0.28
		k (kPa-sec)	18.57	18.93	20.51	23.12	25.45	29.46	33.25	36.82
3622	EPDM-3	n	0.30	0.31	0.28	0.26	0.25	0.24	0.22	0.24
		k (kPa-sec)	13.33	13.19	15.82	19.57	23.42	25.67	32.27	37.80
3761	EPDM-3	n	0.34	0.32	0.31	0.29	0.26	0.24	0.22	0.24
		k (kPa-sec)	9.28	11.38	13.01	15.06	20.51	25.55	33.12	38.85
3761	EPDM-2	n	0.41	0.37	0.37	0.35	0.32	0.25	0.22	0.22
		k (kPa-sec)	4.65	6.42	6.83	8.23	11.08	19.20	27.93	34.79
3181	NR-SBR	n	0.28	0.27	0.28	0.27	0.26	0.25	0.23	0.25
		k (kPa-sec)	33.61	34.79	37.47	42.23	49.04	55.56	68.97	68.27
3429	NR-SBR	n	0.34	0.31	0.30	0.29	0.26	0.24	0.22	0.22
		k (kPa-sec)	13.10	15.20	18.14	21.35	28.72	37.67	49.15	59.53
3622	NR-SBR	n	0.40	0.36	0.34	0.31	0.29	0.25	0.22	0.20
		k (kPa-sec)	5.84	8.61	10.97	13.94	19.01	27.41	38.79	49.84
3761	NR-SBR	n	0.42	0.40	0.38	0.33	0.30	0.26	0.22	0.21
		k (kPa-sec)	4.60	5.23	6.77	10.50	14.30	22.22	32.22	43.24

Also observable in Figure 12 is the role of molecular weight of the PP continuous phase. For both EPDM and SBR blends, *k* increases with the molecular weight of PP as seen in Figures 12(B) and 12(F). Additionally, Figure 12(D) indicates that smaller rubber particle size increases *k*, suggesting that greater interfacial contact area between the two phases retards flow. Also shown in Figure 12 are the corresponding exponents *n*. These decrease with decreasing rubber content indicating greater shear rate sensitivity at higher dispersed phase concentrations. Similar results were previously reported by Romanini and coworkers[33] for four EPDM/PP blends and by Mukhopadhyay and Das[34] for a series of EPDM/polyethylene blends. This sensitivity to shear rate appears less pronounced for higher molecular weight PP [Figures 12(A) and 12(E)] and also decreases with increasing rubber particle size as shown in Figure 12(C).

3.4.2 Reactive Blending

Mechanical properties of the simple blends discussed above were insufficient to meet the requirements of either thermoplastic elastomer or toughened plastics applications. Consequently, it was necessary to employ the reactive blending approach detailed earlier. Figure 13 illustrates the importance of reactive blending through the tensile properties of a series of EPDM-1/PP-4011 blends. Data in Figure 13 represent only one blend family, but are consistent with the other EPDM blends considered. Two observations are readily apparent with respect to the strengths of these EPDM blends. First, the stress capability of the blend decreases as the rubber content goes up. Basically, this can be explained through a volume rule of additivity where the higher strength PP molecules are gradually replaced by the lower strength EPDM phase. Secondly, reactive blending dramatically enhanced the stress capability of all the blends except for those at 10 percent rubber content. Percentages increases as great as 80 percent at the highest rubber content were observed.

Figure 14 shows two possible chemical mechanisms that may occur during reactive blending that contribute to these superior properties. Since the majority of the double bonds in the recycled EPDM are still available even though it is already vulcanized, by adding appropriate reactive agents, those remaining double bonds can be utilized to graft PP onto the rubber particle surfaces. This reaction leads to better compatibilization between the PP and EPDM phases. Additionally, the reactive blending with high rubber content may also promote crosslinking between rubber particles. Both of these postulated mechanisms are detailed in Figure 14.

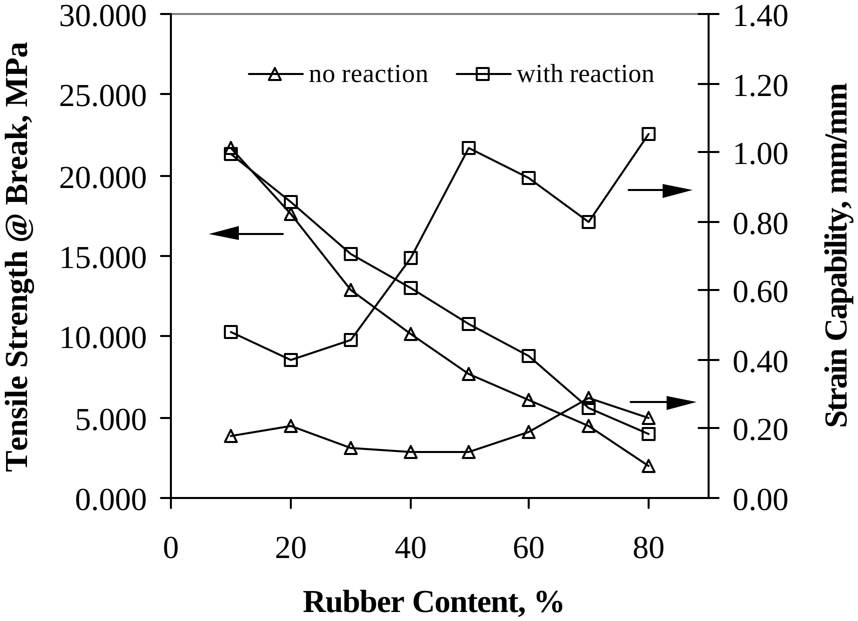


Figure 13. Tensile properties of EPDM-1/PP-4011 blends illustrating effect of reactive blending.

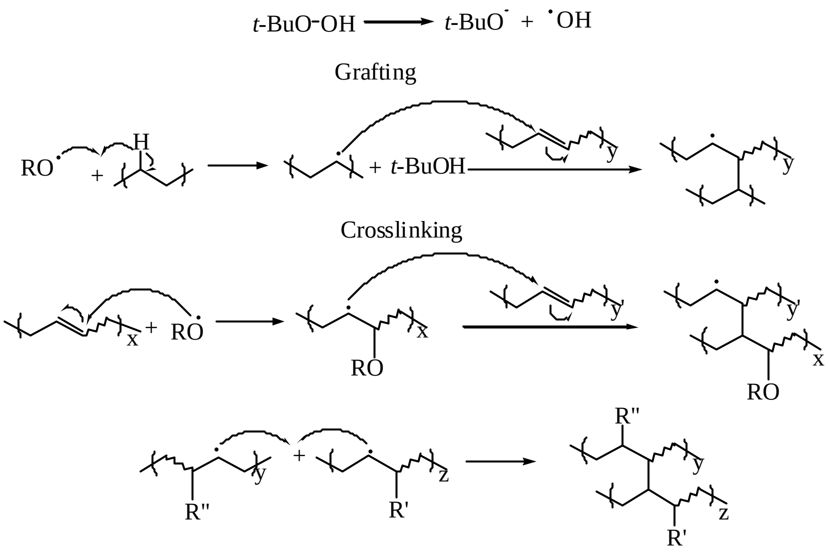


Figure 14. Postulated mechanisms of the free radical reaction.

Previous investigators[10,13,15] demonstrated that similar mechanical properties improvements in EPDM/PP blends could be obtained using maleated PP as a compatibilizer coupled with surface-oxidized rubber. This process involves two pre-reactions both to oxidize the rubber particle surfaces and to maleate the polypropylene. Subsequent reactive blending proceeds in a manner similar to that used for all the blends in this study. Preliminary mixes using the EPDM-1 material with a maleated PP in this investigation showed measurable improvements in properties, but these were not as significant as those shown in Figure 13 and the reaction sequence required substantially more time to complete. Consequently, this approach was discontinued.

Returning to the data in Figure 13, the elongational capabilities that correspond to the breaking stresses discussed above were also considered. Reactive peroxide blending again provided significant improvement in all cases. Samples without reactive blending at high rubber contents did not even provide rubber-like properties. Specifically, elongational capabilities of 105 and 110 percent were obtained for reactive blends at 50 and 80 percent rubber content, respectively. At low rubber levels, strain capability more than doubles with reactive processing. Rubber toughening of the plastic through reactive blending is observed at low rubber contents by the increases in both stress and strain capabilities, which equates to an increase in strain-energy density.

A better understanding for the full range properties investigated was obtained though the nine stress-strain curves plotted in Figure 15. Data in this figure are from the EPDM-3/PP-3761 reactive blend family, indicating both a different source for the recycled EPDM as well as an alternate PP supplier. Stress-strain curves ranged from the flexible plastics response at low rubber content to a high-extension rubbery response at the low PP contents.

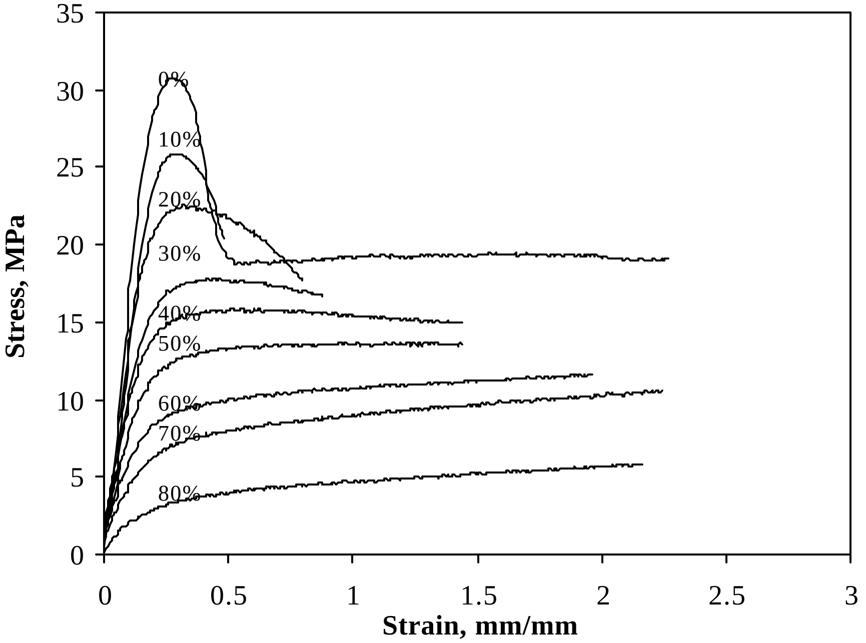
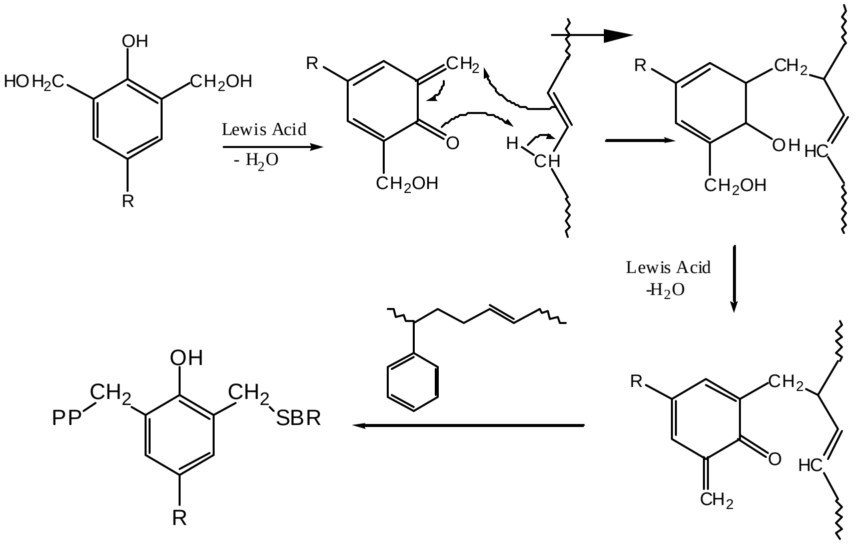


Figure 15. Effect of rubber content on the stress-strain curves for EPDM-3/PP-3761.

As mentioned earlier, other recycled elastomer families were considered as part of this investigation. Figure 16 shows data for SBR/PP-3761 blends over a range of rubber content from 50 to 80 percent by weight. These data are analogous to those for the EPDM blends reported in Figure 13. In all cases, reactive blending again dramatically enhanced mechanical properties. Specific enhancements include an increase in strength from 8 to 19 MPa at 80 percent rubber content, and an increase in elongational capability of approximately 20 percent in all cases. The difference was that in this case reactive blending involved the phenolic material presented earlier rather than the peroxide used with EPDM. A reaction sequence illustrating how this phenolic may react with the butadiene constituent of the SBR is presented in Figure 17. Finally, both reactive blending approaches were tried with the NR/SBR commingled recycled tire rubber, but no significant enhancement in mechanical properties was noted. Additional research will be required before the properties of these recycled rubber blends can be brought to the levels of the other elastomers in this study.



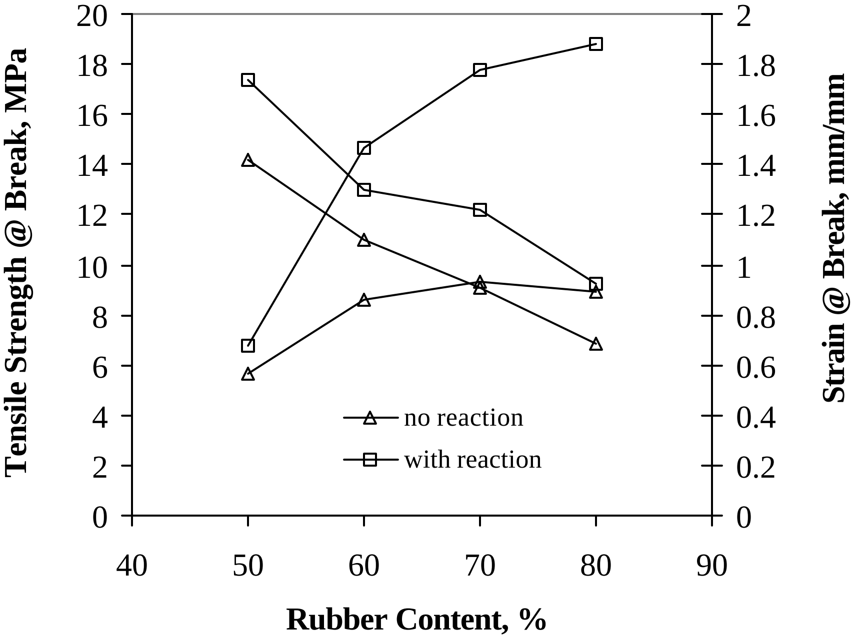


Figure 16 Tensile properties of SBR/PP-3761 blends illustrating effect of reactive blending.

Figure 17. Postulated mechanism for the phenolic compatibilization of SBR/PP blends.

3.4.3 Rubber Particle Size

As mentioned in the Introduction, rubber particle size is known to affect the mechanical properties of recycled rubber/plastic blends. This has been attributed to a reduction in the inherent flaw size of the resultant composite[16,18], or to better interfacial contact[17,19]. Figure 18 presents tensile failure data as a function of rubber content for PP-3761 blended with both EPDM-2 and EPDM-3. These two elastomers are both from the same source and differ only in that EPDM-2 has the finer particle size. Data in this figure shows no significant differences with respect to tensile strength, but a pronounced effect when elongational capability is considered. The smaller particle size enhances strain capability at all rubber concentrations above 40 percent. At the highest rubber concentrations, this improvement is approximately 150 percent. Although significant, these changes in properties do not appear to be sufficient to justify additional costs associated with the finer particle size material, although a cost/properties trade-off study may be appropriate for applications demanding superior properties.

Returning to Figure 12, we also note that the EPDM-2 compounds have lower consistency indices than EPDM-3 compounds suggesting reduced resistance to flow. Similar observations were made by Rajalingam and coworkers[19] with respect to melt flow indices. Figure 12 also shows that the smaller rubber particle size blends have greater shear rate sensitivity as indicated by the higher *n* values. A complete rheological description of these phenomena is not possible at this time; however, these limited data do suggest that at elevated melt temperatures, the rubber phase better compatibilizes with the PP resulting in a blend that flows in a manner that more closely resembles that of the pure PP material.

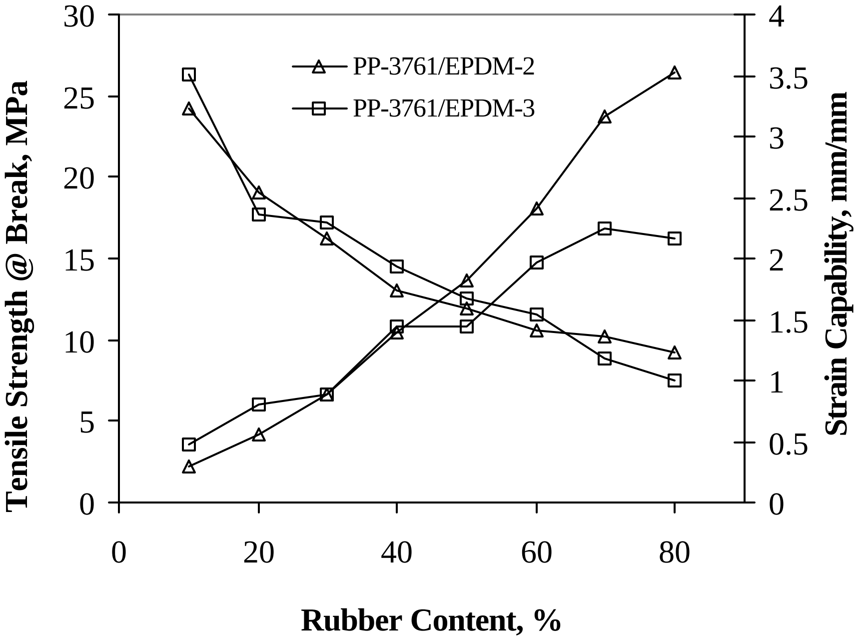


Figure 18. Tensile properties of EPDM-2/PP-3761 and EPDM-3/PP-3761 reactive blends, illustrating the role of recycled rubber particle size

3.4.4 Polypropylene Molecular Weight

Figure 19 presents the results from tensile tests conducted on EPDM-3 blended with four different polypropylenes. The four polypropylenes varied in number-averaged molecular weight M_n from 27 to 84 D as shown in Table 4. Data in Figure 19 show tensile strength generally decreasing with increasing rubber content. The effect of Mn of the PP phase can be seen to increase the strength capability of the blend, particularly for the PP-3181 or highest molecular weight material. More information regarding the influence of hard phase molecular weight can be obtained from considering the elongational capability given in Figure 20. Here a clear ordering is observed with the highest Mn materials having the greatest strain capabilities regardless of rubber content. At the lowest rubber contents, this increase is from approximately 50 to greater than 550 percent, while at the highest rubber contents a more modest increase from 200 to 400 percent is observed.

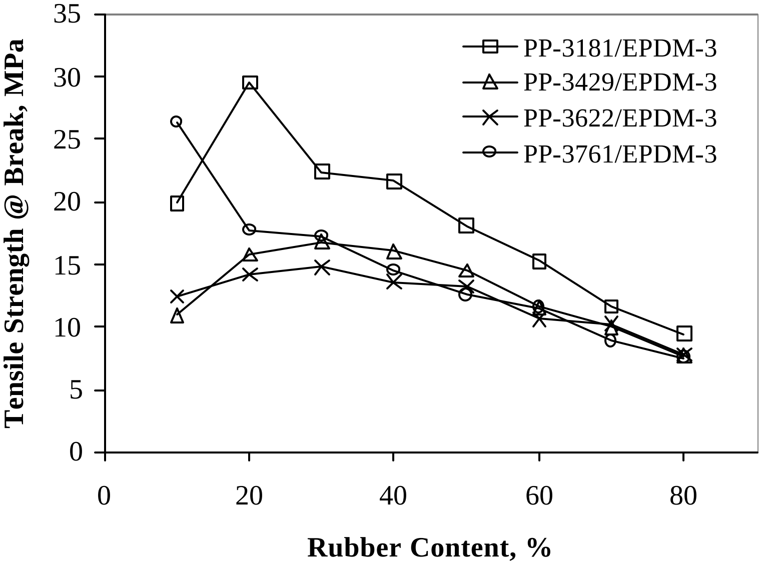


Figure 19. Tensile strength properties of EPDM-3 blended with four polypropylenes of different molecular weights:

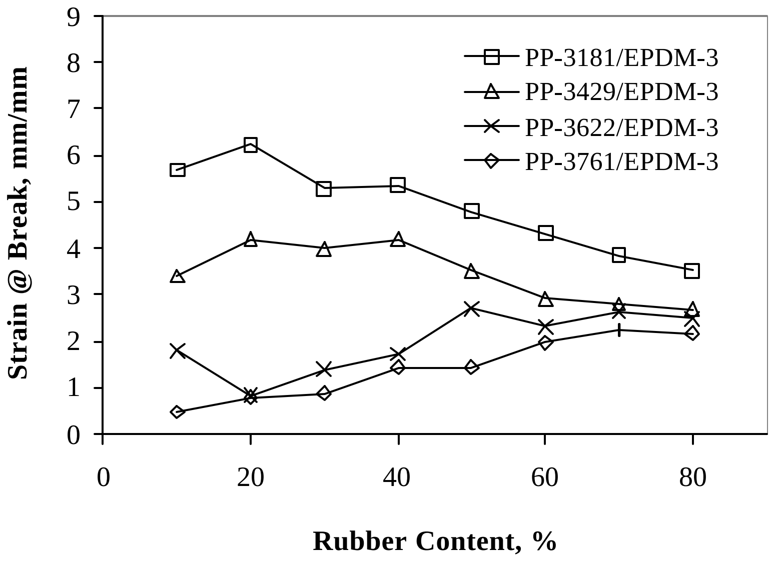


Figure 20. Tensile strain capability properties of EPDM-3 blended with four polypropylenes of different molecular weights

Thermodynamics of mixing arguments[1] suggest that the data in Figure 19 and 20 be interpreted as evidence of greater phase separation behavior in the higher molecular weight polypropylene systems. Also to be considered is the percent crystallinity within the hard phase. These data are shown in Figure 21 for the same blends at representative rubber concentrations. Crystallinity is seen to decrease with both increasing rubber content and molecular weight of the PP. These data suggest poorer ordering within the semi-crystalline phase owing to a higher degree of intermingling with the amorphous rubber phase, or the higher melt viscosities that were shown earlier in Figure 12. Additional support for this conclusion comes from comparison of the original crystallinities of the polypropylenes in Table 4 with those reported in Figure 21. A more dramatic decrease in crystallinity is noted for the lower molecular weight materials. Finally, Figure 22 shows the effect of reactive blending on the crystallinity of the hard phase in the EPDM-1/PP-4011 blend. Reactive blending lowers percent crystallinity in all cases presumably by decreasing the ability of individual molecules to participate in the growth of crystallites.

Figure 23 presents tensile data for simple blends of NR/SBR with each of the four different molecular weight polypropylenes as functions of rubber content. Here an ambivalent role of PP M_n is obtained from the tensile strength data; however, a clear ordering with respect to molecular weight as noted in Figure 20 is again apparent. The higher molecular weight polypropylenes provide enhanced elongational capabilities.

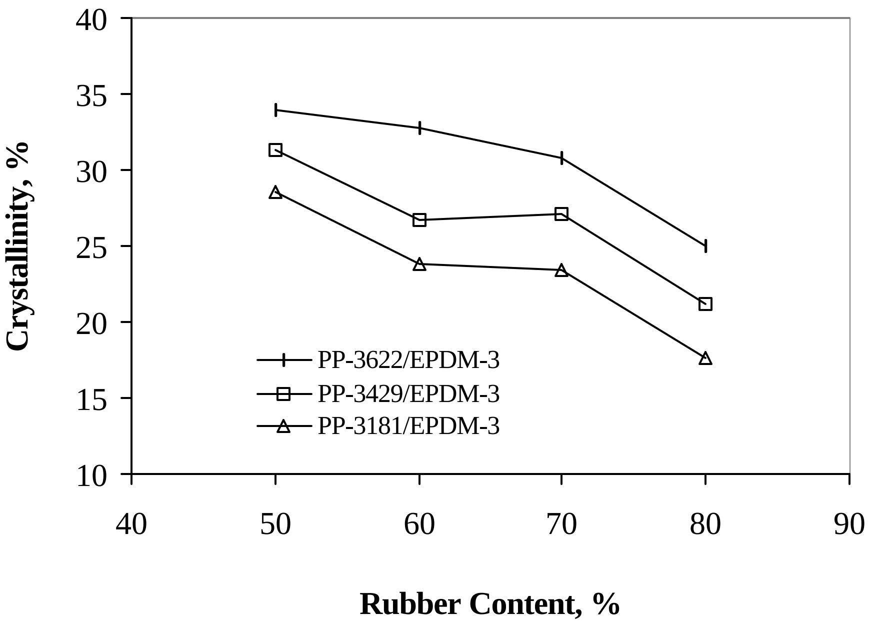


Figure 21. Percent crystallinity measurements for the indicated polypropylenes after blending with the EPDM-3 recycled rubber.

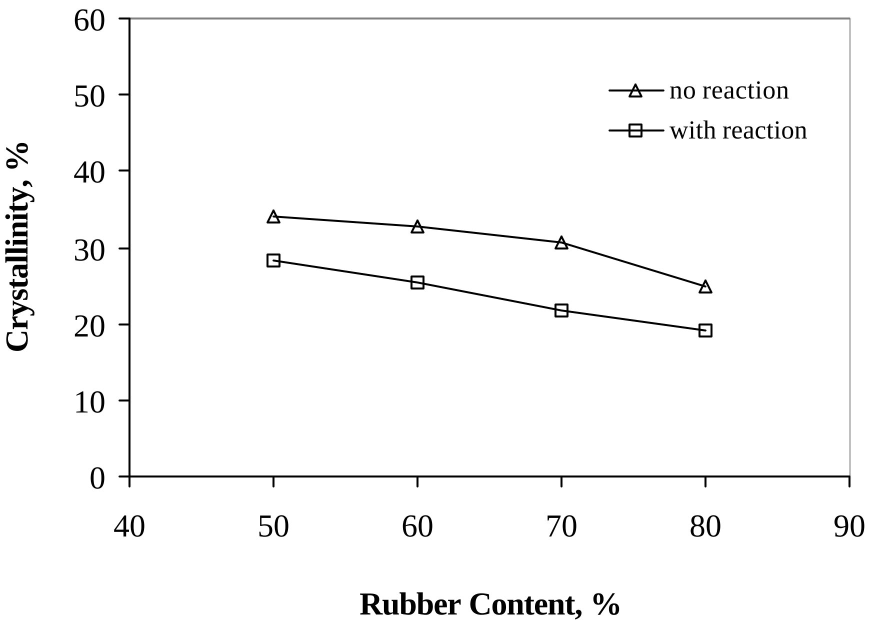


Figure 22. Percent crystallinity measurements for the EPDM-1/PP4011 blend showing effects of both reactive and simple blending.

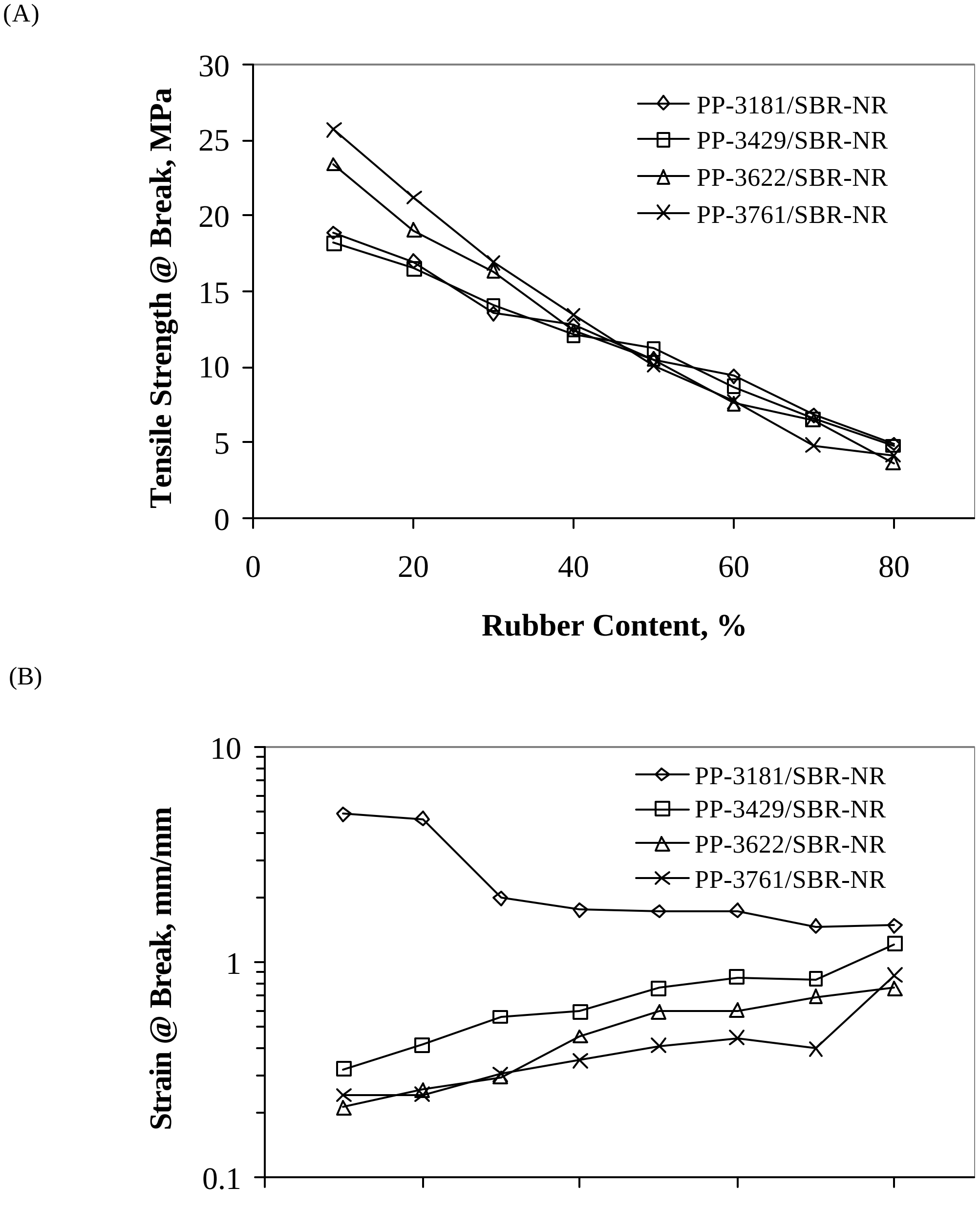


Figure 23. Tensile properties of recycled SBR/NR blended with four polypropylenes of different molecular weights: (A) tensile strength and (B) strain capability.

3.5 Conclusions

The following conclusions are drawn from the investigation reported in this paper:

1. Rheological investigations of the recycled rubber/plastic blends considered indicate that the blends are two-phase systems with the plastic material serving as the continuous phase. Capillary rheometer data shows that the blends are more sensitive to shear at higher rubber loading fractions, and the power law exponent generally decreases with polypropylene molecular weight and increases with recycled rubber particle size. Correspondingly, the consistency index increases with rubber content and PP molecular weight, and decreases with rubber particle size.
2. Mechanical properties of the rubber/plastic blends are not sufficient for most engineering applications without some form of compatibilization. Two reactive blending techniques were successfully demonstrated during this study for enhancing mechanical properties. A peroxide reaction was used for the recycled EPDM/PP blends and a phenolic reaction employed for recycled SBR/PP blends.
3. Smaller particle sizes of the recycled elastomers were observed to improve mechanical properties of the resultant blends; however, the improvement was not considered significant when the additional costs associated with size reduction operations are included.
4. The molecular weight of the polypropylene was found to strongly influence properties in blending with both EPDM and SBR/NR. Higher molecular weight in hard phase increased both tensile stress and elongational capability. These results are explained in terms of greater phase separation resulting in a smaller impact on the crystallization processes within the PP.

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4 COMPATIBILIZATION APPROACHES FOR RECYCLED RUBBER/THERMOPLASTIC BLENDING[*]

4.1 Abstract

This research investigated the use of recycled passenger tire rubber as a blending component for the development of novel thermoplastic elastomers (TPE) and rubber-toughened plastics. The recycled rubbers were obtained from two commercial sources and included styrene-butadiene rubber (SBR), and a commingled mixture of this material with natural rubber (NR). A series of different molecular weight polypropylenes (PP) and an ethylene-octene copolymer (EOC) were used as the plastic/continuous phase. Blends were prepared in a Haake Buechler batch mixer over a broad range of constituent fractions. Two compatibilization techniques, one based on a Freidel-Crafts approach and the other utilizing a phenolic resin reaction, were used to improve the quality of the scrap rubber/plastic blends with respect to both mechanical and rheological properties. Data indicate that these compatibilization techniques are required to obtain acceptable mechanical strength in the resultant materials. Rheological results indicate that the plastic component remains the continuous phase over a range of rubber loading fractions from 10 to 80 percent by weight. Use of EOC as the plastic phase resulted in softer (64-77A) TPEs with greater than 1000 percent elongational capability. Increasing the molecular weight of the harder (20-38D) PP blends provided enhancements in both stress and strain capability.

4.2 Introduction

Blending recycled rubber with other materials has been an attractive alternate to disposal methods for many years. Its chief drawback has been the difficulty in obtaining adequate properties from the resultant blends. Early research[1-5] demonstrated that the incorporation of recycled rubber into either virgin rubber or plastics resulted in materials with inferior properties. This has limited the use of this potentially beneficial technology, even as a greater understanding for the role of rubber particle size and surface reactivity has been developed[2-3,6-8]. As a result, a number of compatibilization and modification techniques have been investigated[1-2,5,9-14]. Further complicating the issue is the wide variety of recycled rubber compounds and, in many cases, their inherent commingled nature. Consequently, it is often necessary to modify the blending operation for each specific recycled rubber received.

Recycled rubber/thermoplastic blending technology has been built upon the science developed for the manufacture of thermoplastic elastomers[15] and rubber-toughened plastics[16] from virgin materials. These fundamental studies have provided the criteria for a successful blend. The first requirement is that the two components be

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[*] H.S. Liu, J.L. Mead, and R.G. Stacer, “Compatibilization Approaches For Recycled Rubber/Thermoplastic Blending”, presented at a meeting of the Society for Advancement of Materials and Process Engineering (SAMPE) September 2000.

thermodynamically incompatible enough to phase separate, but not so dissimilar that intimate intermixing cannot be accomplished[15,17-21]. In a successful blend the domain size of the dispersed phase is small and interfacial surface area is maximized, a requirement that can only occur within certain limits of the solubility parameter difference between the two materials in the blend[15,17,19,21]. Crosslinking of the rubber phase through processes such as "dynamic vulcanization" is often a second requirement to reduce creep in TPEs and enhance the strength of toughened plastics[15-17]. In cases where the solubility parameter mismatch may be large, compatibilizers that act as interphase bridges between hard and soft phases are often required[22-27].

The objective of this research was to develop an approach for producing novel TPEs and toughened plastics from blends of PP or EOC with styrene-butadiene rubber (SBR) and natural rubber (NR). These two rubbers are the two most common elastomers used in the United States by volume[28]. Two compatibilization approaches were used to improve the resultant blend properties. Quantification of the important structure-property relationships of the blends and the critical rheological parameters was made where possible. The details of the compatibilizers and their proposed mechanism are also presented.

4.3 Experimental

4.3.1 Materials

Table 6 presents characterization data for the recycled rubber compounds considered. They comprise one SBR compound and an NR/SBR commingled mixture, obtained from the listed commercial sources. Particle size reduction was accomplished by the commercial sources using ambient temperature underwater processing. Reported particle sizes were converted from the mesh sizes provided by the processors.

Table 6. Recycled Rubber Characterization Data

Material	Supplier	Source	Particle Size (μm)	ρ (g/cc)
SBR	Erickson	Tire	89	1.13
NR/SBR	Rouse	Tire	89	1.14

Table 7 lists the four polypropylenes and the ethylene-octene copolymer (poly α-olefin) investigated as part of this study. The polypropylenes represent a series of different of molecular weights, as well as including samples from two different sources. Earlier studies[5,14] indicated that melt-flow index of PP played a critical role in the properties of recycled EPDM elastomers/PP blends. Consequently, a broad range of molecular weights was selected for this investigation. Characterization data for this series of PPs was previously reported[14].

Table 7. Characterization Data for Polypropylenes

Material	Supplier	M_n (D)	M_w/M_n	T_m (°C)	Crystallinity (%)	σ_b (MPa)	σ_y (MPa)	ε_b (%)
PP-3181	Fina	84	6.1	172	30	41	30	760
PP-3429	Fina	40	7.0	171	42	44	32	844
PP-3622	Fina	29	6.6	173	55	28	32	672
PP-3761	Fina	27	7.4	171	59	16	32	528
EOC	Dow	-	-	60	-	16	-	750

Chemical compatibilizers used in this study were tin chloride (formula: $SnCl_2$) from Aldrich Chemical Co. and SP-1045 (heat reactive octylphenol-formaldehyde resin which contains methylol groups) from Schenectady International Inc.

4.3.2 Blending

Batch mixing was performed in a torque rheometer (Haake Buechler Rheocord System 40). The mixer was preheated to the mixing temperature, 200°C, until stable. The rotor speed was set at 30 rpm and PP added. The rubber component was added once the PP was completely melted as indicated by a stabilized torque reading. SBR/PP and NR-SBR/PP blending using SP-1045 shall be referred to as reactive blending throughout this discussion. Similar blend processing using this approach was previously reported by Coran and Patel[29]. SBR/PP and NR-SBR/PP blending using tin chloride shall be termed Freidel-Crafts processing. The tin chloride was added to the blend during the rubber addition cycle.

4.3.3 Characterization and Properties Testing

Dynamic mechanical analysis (DMA) was carried out in forced dynamic shear using a rectangular torsion specimen in a Rheometrics 605. Specimens were sheared at a frequency of 1 Hz with an amplitude of 0.2 percent. Temperature sweeps were performed over the range from –100 to 50°C with a heating rate of 3°C/min. Reported T_g values were obtained from the maximum in the shear loss modulus G" curves.

Apparent viscosities η were measured using a capillary rheometer (Kayeness, Galaxy IV) at 200°C using a die with an L/D ratio of 10/1. Flow curves were generated from data collected at nine different shear rates ranging from 10 to 5000 s^{-1}. Data were reduced using a two-parameter power law equation

$$\eta = k\left|\frac{\dot{\gamma}}{\dot{\gamma}_o}\right|^{n-1} \tag{3}$$

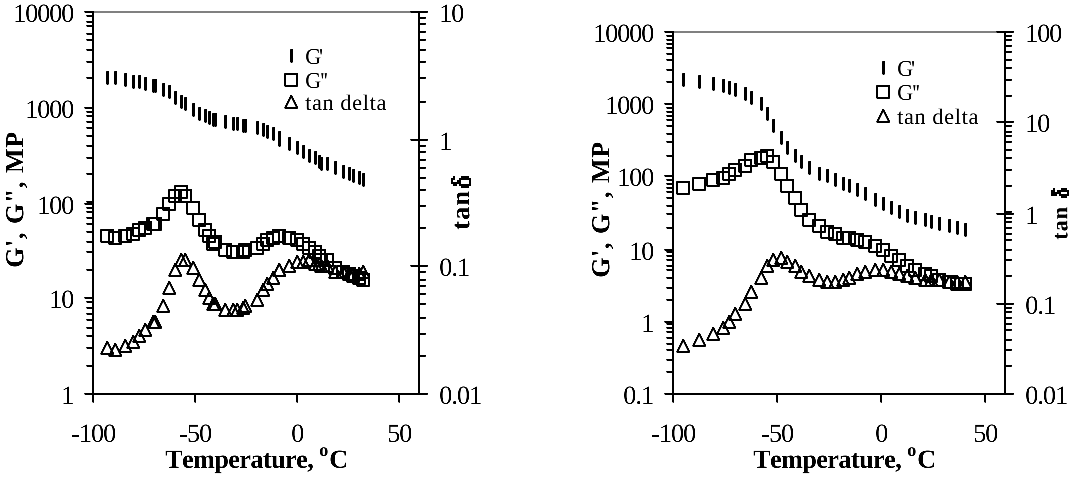
where k is the consistency index, n is the power law exponent, and $\dot{\gamma}$ and $\dot{\gamma}_o$ represent the shear rate and a reference shear rate of 1 s^{-1}, respectively.

Tensile specimens from compression-molded sheets were prepared using a half scale ASTM D638 (die D). Tensile testing was performed with an Instron 6025 and a crosshead speed of 50 mm/min. Strain was determined from the change in effective gage length by optical methods.

4.4 Results and Discussion

4.4.1 Rheological Data for Simple Blends

Dynamic mechanical properties data in the form of temperature sweeps for two simple blends are collected in Figure 24. By simple blends, we refer to a blend in which reactive blending or Freidel-Crafts processing was not accomplished. Properties presented in these curves are shear storage modulus G’, shear loss modulus G”, and their ratio tan δ = G”/G’. Recycled SBR blended with a high-flow polypropylene (PP-3761) at two rubber weight fractions of 50 and 80 percent are shown in this figure.



(A) **(B)**

Figure 24. Dynamic properties data for simple blends: (A) 50% SBR/PP-3761, and (B) 80% SBR/PP-3761.

Evidence of phase separation was revealed in all cases as two temperature dispersion peaks in both G” and tan δ curves. The low temperature peak between –55 and –56°C is indicative of the glass transition temperature of the SBR rubber, while the peak slightly below 0°C is due to the T_g of the PP phase. Both G’ curves reach a glassy plateau at approximately 2 GPa, which appears to be independent of rubber content. As temperature increases, however, G’ enters the transition region, which is more distinct for the blends containing 80 percent rubber. At the highest temperatures, G’ reaches a rubbery plateau of approximately 100 MPa for the blend with 50 percent rubber and 10 MPa for the higher rubber content blend.

Flow curves for simple NR-SBR/PP blends were generated using a capillary rheometer as discussed earlier. Rubber weight content was varied from 10 to 80 percent. Figure 25 presents the flow curves for eight blends at various rubber contents. A strong pseudoplastic behavior is observed in all cases. Similar data were collected for all 32 rubber/plastic blends considered and were reduced by Equation [3]. The resulting power law exponents, *n*, and consistency indices, *k*, are shown in Table 8. In order to illustrate the distinct behaviors within the SBR blends, the power law exponents and consistency indices are also plotted as functions of rubber content [Figure 26 (A) and Figure 26 (B)].

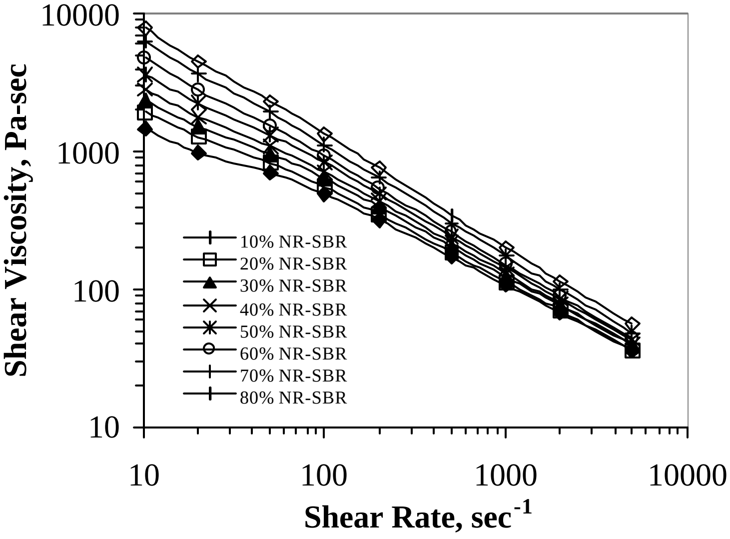


Figure 25. Representative flow curves for NR-SBR/PP-3761 at eight rubber fractions.

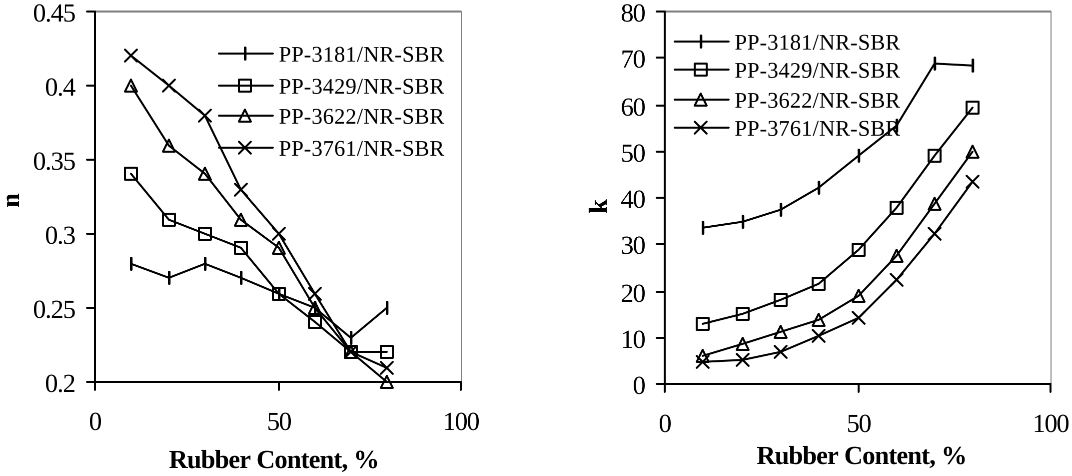
With an increase in rubber content n generally decreases, while k increases. An increase in *k* with the crosslinked rubber content is consistent with the general theory for the rheology of suspensions, where the resistance to flow of a composite increases exponentially with content of the dispersed phase. In this case, the carbon black filled and crosslinked elastomer acts as the dispersed solid in the continuous phase of PP melt. The increase in the viscosity of our blends is not as pronounced as expected for rigid solid fillers, a feature believed attributable to the deformable nature of the rubber particles. The effect of PP molecular weight on the rheological behavior of the blends is indicated in Figure 26. For all blends, *k* increases with increasing PP molecular weight [Figure 26(B)]. Figure 26 also shows a decrease in the power law index with an increase in the rubber content, indicating greater shear rate sensitivity at higher dispersed phase concentrations. Similar results were reported by Romanini and coworkers[30] for four EPDM/PP blends, by Mukhopadhyay and Das[31] for a series of EPDM/polyethylene blends, and by Liu and coworkers for recycled EPDM/PP blends[14]. This response to the shear rate appears less appreciable for higher molecular weight PP [Figure 26(A)].

Table 8. Power-law Exponents and Consistency Indices of NR/SBR-PP Blends

PP	Rubber		Rubber Content, %							
			10	20	30	40	50	60	70	80
3181	NR-SBR	n	0.28	0.27	0.28	0.27	0.26	0.25	0.23	0.25
		K (kPa-sec)	33.61	34.79	37.47	42.23	49.04	55.56	68.97	68.27
3429	NR-SBR	n	0.34	0.31	0.30	0.29	0.26	0.24	0.22	0.22
		K (kPa-sec)	13.10	15.20	18.14	21.35	28.72	37.67	49.15	59.53
3622	NR-SBR	n	0.40	0.36	0.34	0.31	0.29	0.25	0.22	0.20
		K (kPa-sec)	5.84	8.61	10.97	13.94	19.01	27.41	38.79	49.84
3761	NR-SBR	n	0.42	0.40	0.38	0.33	0.30	0.26	0.22	0.21
		K (kPa-sec)	4.60	5.23	6.77	10.50	14.30	22.22	32.22	43.24

4.4.2 Blend Compatibilization

Mechanical properties of the simple blends, as indicated in Figure 28, were insufficient to meet many of the application requirements for either thermoplastic elastomers or rubber-toughened plastics. Consequently, it was necessary to employ a compatibilization approach. In this study, two approaches were investigated to improve the properties of the resulting blends through the formation of interfacial bridges between the rubber and the PP. Specifically, the first method was to graft PP to the benzene ring in the SBR rubber through the use of Friedel-Crafts processing, and the other was to adopt the reactive blending method originally developed for nitrile rubber (NBR) blends[29].



(A) **(B)**

Figure 26. Reduced power law exponents (A) and consistency indices (B) as functions of rubber fraction for NR-SBR/PP simple blends.

4.4.2.1 Friedel-Crafts Processing

Friedel-Crafts is a classic organic reaction for addition to aromatic compounds. By exploiting this reaction, it was expected that chains of the thermoplastic material might graft onto the SBR phenyl group to produce an interfacial bridge. Figure 27 illustrates the postulated reaction pathway. In the presence of a Lewis acid, such as tin chloride, the vinyl moiety in the PP chain is activated, offering the potential for grafting with the rubber phase through the aromatic ring in SBR.

Several different Lewis acids where investigated as a part of this study; aluminum chloride, tin chloride, and iron chloride. Aluminum chloride produced a very aggressive reaction, which resulted in a hard and brittle material. In the case of iron chloride, the hydroscopic nature of this material made processing difficult and resulted in its use being discontinued. Only tin chloride produced blends with improved properties. Figure 28 illustrates the tensile rest results from the reactive blending with a concentration of 0.2 percent $SnCl_2$ in blends of SBR-NR and PP-3622. As indicated in Figure 28, the stress capability of the blends decreases as the rubber content is increased. This observation can be explained by the gradual substitution of the higher strength PP molecules with the lower strength rubber phase. This compatibilization approach seems to provide little improvement to the breaking strength of all the blends, but did improve the breaking strain when compared to the untreated blends. Specifically, the elongational capabilities for reactive blends were improved more than 50 percent, except in the case of blends with 10 percent rubber content. Increasing the concentration of tin chloride from 0.2 to 2 percent did not result in further improvements; in fact, the blends showed poorer properties than at the lower concentration. The use of Friedel-Crafts processing does enhance the properties of the blends, but under the conditions reported here, these improvements are rather limited compared to the reactive blending approach described below.

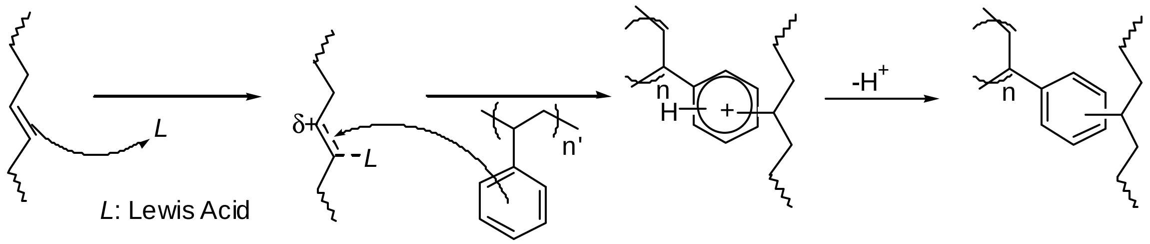


Figure 27. Postulated mechanism for the Friedel-Crafts processing of SBR /PP.

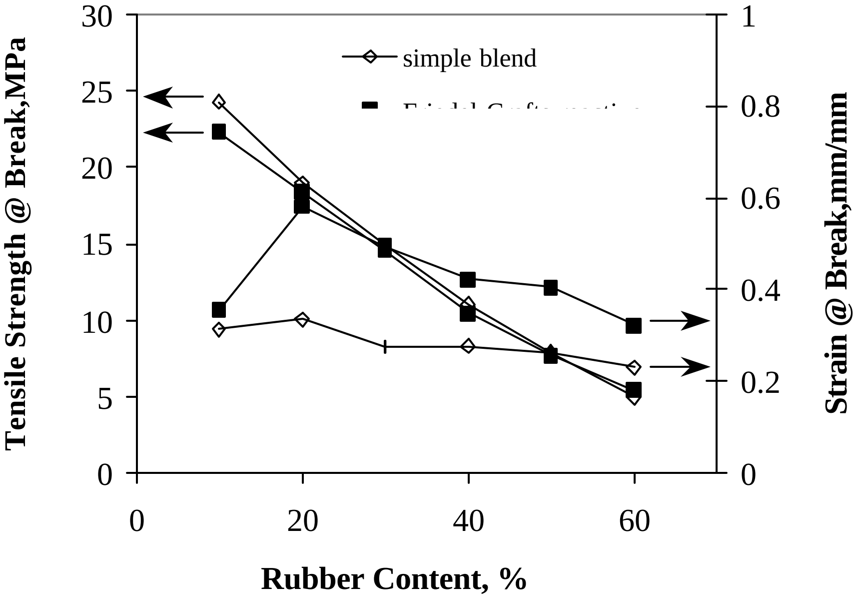


Figure 28. Tensile properties of NR-SBR/PP-3622 blends illustrating effect of Freidel-Crafts processing.

4.4.2.2 Reactive Blending

The second compatibilization approach investigated was adopted from work on the dynamic vulcanization of PP/NBR blends[29]. The phenolic curing reaction was expected to again provide interfacial bridges between SBR and PP as depicted in Figure 29. Figure 30 shows data for SBR/PP-3761 blends over a range of rubber content from 50 to 80 percent by weight. Similar to the results for Friedel-Crafts processing, stress capability decreases as the concentration of rubber goes up. In this case, however, the reactive blending more dramatically enhanced mechanical properties in all cases. Tensile strength increased 6 to 9 MPa at 80 percent rubber content, and an increase in elongational capability of approximately 60 percent was observed independent of rubber content.

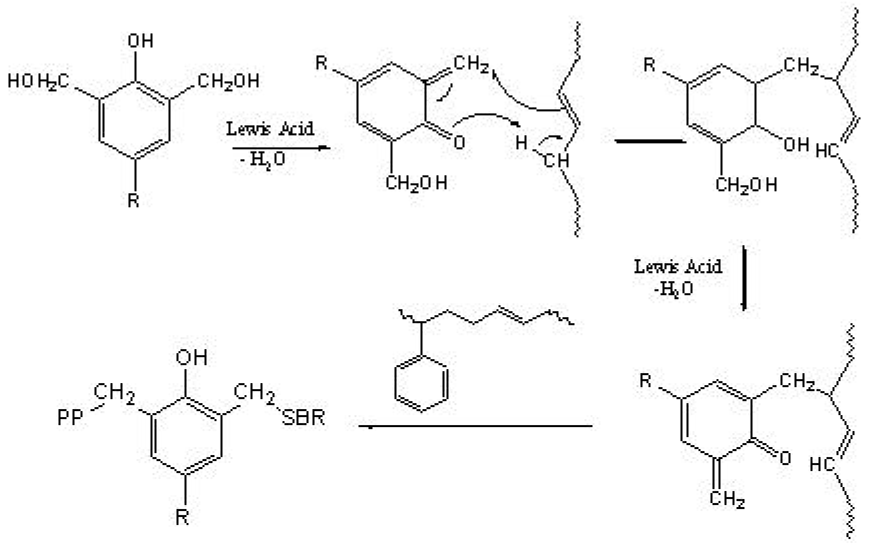


Figure 29. Postulated mechanism for the reactive blending mechanism for SBR/PP.

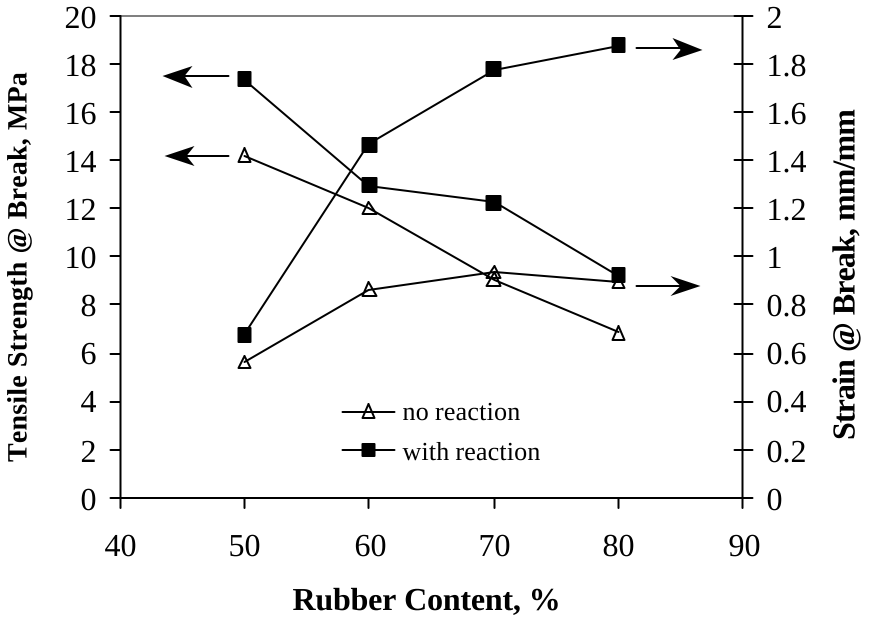
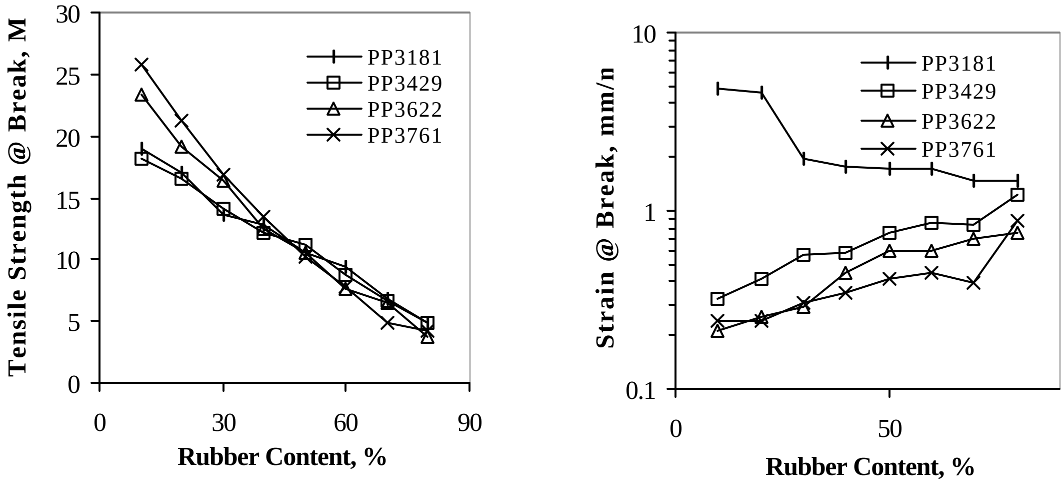


Figure 30. Tensile properties of SBR/PP-3761 illustrating reactive blending.

4.4.3 Polypropylene Molecular Weight

Figure 31 presents results from tensile tests conducted on NR/SBR blended with the four polypropylenes. These varied in number-average molecular weight, Mn, from 27 to 84 D as shown previously in Table 7. Reactive blending was accomplished on each of these systems prior to tensile testing. As expected, the data in Figure 31 show that the tensile strength generally decreases with an increase in rubber content. Higher values of Mn also significantly increase the strength capability of the blend, particularly for the PP-3181, the polypropylene with the highest molecular weight. More information regarding the effect of the molecular weight of hard phase can be obtained by considering the elongational capability, also shown in Figure 31. It can be clearly seen that materials with the highest M_n have the greatest strain capabilities, regardless of rubber content. At the lowest rubber contents, the increase in strain capability is from approximately 30 to above 500 percent, while at the highest rubber content, increases ranging from 80 to 150 percent are observed.



(A) **(B)**

Figure 31. Tensile properties of recycled SBR/NR blended with four polypropylenes of different molecular weights: (A) tensile strength and (B) strain capability

Thermodynamics of mixing arguments suggest that the data in Figure 31 should be interpreted as an evidence of greater phase separation behavior in the higher molecular weight polypropylene systems. Also to be considered is the percent crystallinity within the hard phase. These data suggest a poorer ordering within the semi-crystalline phase owing to a higher degree of intermingling with the amorphous rubber phase in the blends containing lower molecular weight PP. Prior work with PP/EPDM scrap rubber blends indicated that percent crystallinity (as measured by differential scanning calorimetry) decreased with increasing molecular weight of PP[5,14]. Reactive blending schemes acted to further decrease the percent crystallinity above that of the simple blends. A reduction in the percent crystallinity as the PP molecular weight increases is the most probable explanation for the effect of PP molecular weight on the properties of the blends.

4.4.4 Choice of Hard Phase Materials

As previously mentioned, an additional polyolefin was evaluated as part of this effort to provide softer blends. The Shore hardness values of the blends reported thus far ranged from 20 to 38 on the Shore D scale. These values are too high for many applications. As a result, blends with EOC (poly α-olefin) were also evaluated. Illustrative tensile properties for simple blends of this material with SBR/NR, along with corresponding curves for NR-SBR/PP-3622, are given in Figure 32. NR-SBR/EOC blends ranged in hardness from 64 to 77 on the Shore A scale.

Figure 32 again shows that simple blends utilizing polypropylenes have inferior properties unless some type of compatibilization reaction is accomplished. Note the low strain capabilities, which stay far below 100 percent regardless of rubber content. When EOC is substituted for PP, an increase in strain capability of almost two orders of magnitude is readily apparent, even in the absence of reactive blending. Correspondingly, however, tensile strength is approximately one-half of the PP value at rubber contents between 10 and 30 percent, and is still significantly lower at the other fractions. This highlights the trade-off in strength that is required to obtain softer materials. The reason these EOC blends are weaker can be understood by considering the strength of the thermoplastic resin by itself. Table 7 shows that the stress capability of EOC is 16 MPa, which can be compared with 28 MPa for PP-3622. When the lower strength capability recycled rubber is blended into these two thermoplastics, the strength of the resultant blend decreases in a linear fashion following a simple volumetric rule of additivity. Simple behavior can be observed by reviewing the stress capability curves in Figures 28, 30 and 31. Additional research would be required to determine if the compabilization approaches taken for the PP blends in this study could also be employed to enhance the strength of their EOC counterparts.

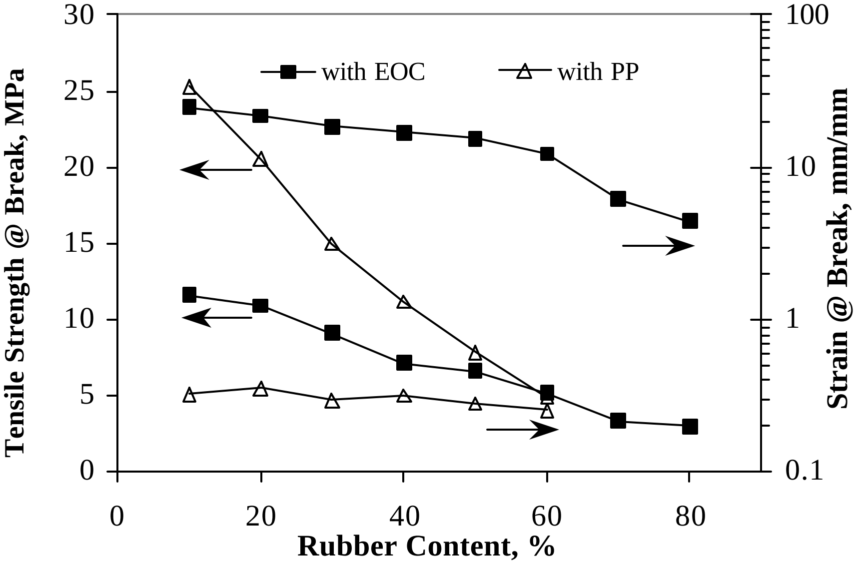


Figure 32. Tensile properties of NR/SBR blend with different thermoplastics materials.

4.5 Conclusions

The following conclusions are drawn from the investigation reported in this paper:

1. Rheological studies of the recycled rubber/plastic blends considered indicate that the blends are two-phase systems with the plastic material serving as the continuous phase. Capillary rheometer data shows that the blends are more sensitive to shear at higher rubber loading fractions, and the power law exponent generally decreases with an increase in polypropylene molecular weight. Correspondingly, the consistency index increases with rubber content and PP molecular weight.
2. Mechanical properties of the rubber/plastic blends are not sufficient for most engineering applications without some form of compatibilization. Two blending techniques were successfully demonstrated during this study for enhancing mechanical properties. Of the two techniques, the reactive blending approach using a phenolic compatibilizer showed the most significant improvement in properties. Additionally, substitution of an EOC (poly α-olefin) material for PP was also found to increase the strain capability of the resultant blends.
3. The molecular weight of polypropylene, when used as the hard phase, was found to strongly influence properties in blending with SBR/NR scrap rubber. Higher molecular weight PP increased both tensile stress and elongational capability. These results are explained in terms of the crystallization processes within the PP.
4. Blends prepared from polypropylene possessed hardness values at the high range of those generally associated with dynamically vulcanized TPEs. Softer materials were obtained by replacing PP with EOC

4.6 References

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5 CONTINUOUS VERSUS BATCH PROCESSING OF RECYCLED RUBBER AND PLASTICS BLENDS[*]

5.1 Abstract

An experimental investigation has been conducted using recycled rubber and plastics blends to evaluate processing scale-up from laboratory batch mixers to continuous, twin-screw extruder operations. Recycled elastomers were obtained from commercial sources, and included EPDM rubber of various particle sizes from roofing compounds and a commingled NR/SBR material from tire scrap. These were blended over a range of concentrations with virgin polypropylenes to produce novel thermoplastic elastomers and rubber-toughened plastics. Processing was accomplished using both simple blending and reactive processing approaches. Data indicate that batch mixing provides superior dispersion of the rubber particles in the plastic matrix as quantified by intensity of segregation measurements. Mechanical properties of the resultant blends prepared via corotating twin-screw extrusion, however, could approach those of their batch mixed counterparts if average residence time in the extruder coincided with that of the batch mixing time. Additional adjustments were required to scale-up the reactive blends suggesting a need for greater quality control when processing reactive blends from recycled elastomer streams.

5.2 Introduction

Blending of recycled elastomers with plastics is a promising approach for developing new families of thermoplastic elastomers and rubber-toughened plastics[1-8]. Most investigators[1-5,7-8] have employed compatibilization methods and reactive processing techniques since simple blending with recycled elastomers generally retards mechanical properties[1-2,7-10]. Problems arise, however, with the large variety of elastomeric compounds that are found in a typical recycled rubber stream. Since many of the blending approaches involve chemical reactions or are sensitive to temperature/shear history, scale-up from laboratory batch mixers to continuous processing operations has been challenging[11]. Additionally, reactive processing schemes often require modification or substantial revisions when transitioning to twin-screw extrusion or when the recycled elastomer feed stock is changed.

Control of dispersed phase particle size is critical in obtaining adequate properties when blending for thermoplastic elastomers or rubber-toughened plastics[12-16]. Optimum properties for dynamically vulcanized blends are generally observed with a rubber particle size in the range of one micron[15-16]. This is extremely difficult to achieve using recycled elastomers since the cost of reducing crosslinked rubbers to this size range is prohibitive[1,5,17-18]. Also, dispersion of the recycled rubber in the continuous phase is

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[*] H.S. Liu, J.L. Mead, and R.G. Stacer, "Continous vesus Batch Processign of Recycled Rubber and Plastics Blends", presented at a meeting of the Rubber Division, American Chemical Society, Cincinnati, Ohio, October 2000.

complicated by the fact that during processing the particles stretch, shear, and recover their original shape. Small internal batch mixers, which can quickly grind glass marbles into finely divided powders, allow these problems to be addressed on a laboratory scale. For continuous processing on an industrial scale, corotating twin-screw extruders with intermeshing screw elements appears to provide the best, practical alternative[19-20].

The understanding and ability to model twin-screw extrusion operations has increased dramatically in recent years[19,21-26]. These investigations provide important benchmarks for efforts to scale-up multi-phase polymeric blends from laboratory batch processing. Especially noteworthy is the ability to program the screw geometry to obtain a desired residence-time distribution[21,23-24], as well as the capability of predicting mixing efficacy of various element combinations[25-26]. Both of these parameters are more important in reactive processing than traditional characterization values such as temperature, pressure, and shear stress.

The purpose of this paper is to report on an effort to scale-up blends of recycled rubber and plastics for use as thermoplastic elastomers or rubber-toughened plastics. Resultant blends are characterized with respect rheological properties relevant to processing, phase morphology, and mechanical properties. Development of specific formulations, reactive processing approaches, and optimization of rheological and mechanical properties were previously reported[7-8,27].

5.3 Experimental

5.3.1 Materials

Powdered EPDM elastomers (80 and 170 mesh) were provided by Rouse Rubber from recycled roofing compounds. Additionally, a commingled NR/SBR powder (80 mesh) from tire scraps was obtained from the same source. Particle size reduction was accomplished by Rouse Rubber using ambient temperature underwater processing. Reported particle sizes were converted from the mesh sizes provided by the processor. A density of 1.14 g/cm^3 for these rubbers was previously reported[8]. The polypropylene used in the study came from Fina Oil & Chemical Co. It is identified by the manufacturer as PP-3622, with a melt flow index of 12 g/10 min, a number-average molecular weight of 29 kD, and a polydispersity index of 6.6. Characterization[8] of the polymer showed it to be 55 percent crystalline with a melting temperature of 173^{o}C. Its breaking and yield stresses were 28 and 32, respectively, with an elongational capability of 672 percent[8].

Chemical additives used in this study were *t*-butyl hydroperoxide from Aldrich Chemical Co. *t*-Butyl hydroperoxide was chosen based on its half life of initiation at processing temperature, 200^{o}C, and used as radical initiator during reactive EPDM/PP blending.

5.3.2 Blending

Batch mixing was performed in a torque rheometer (Haake Buechler Rheocord System 40). The mixer was preheated to the mixing temperature, 200^{o}C, until stable. This usually took approximately 30 to 45 minutes. The rotor speed was set at 30 rpm.

Optimization of these parameters with respect to mechanical properties of EPDM/PP blends was accomplished using a six factor/two level design of experiment scheme[7]. The rubber component was added when the PP was completely melted as indicated by a stabilized torque reading. In the case of EPDM/PP reactive blending, the rubber particles were allowed to imbibe the chemical additive at room temperature prior to addition to the mix. Blends prepared without the use of the chemical additive are referred to as simple blends throughout this narrative. All reported rubber contents are by weight.

Processing scale-up of the above materials was performed in a co-rotating intermeshing twin-screw extruder (Werner & Pfleiderer) with a screw diameter of 32 mm and a length of 890 mm. The screws were programmed for a general shear profile. The barrel temperature profile for all blends was 174, 210, 228, and 230^{o}C, with a die temperature of 228^{o}C. A target output of 10kg/hr was maintained using a baseline 250 rpm (starve feeding) with slight variations due to surging and feeder bridging. The screw speed was reduced to 30 rpm to match the residence time of the batch mixer, along with a corresponding reduction in hopper feed rate to maintain an equivalent channel fill fraction. Additionally, the temperature profile was also reduced to more closely approximate batch processing. The new temperature profile corresponding to the zones and die above are 170, 190, 200, 200, and 210^{o}C, respectively. Reported residence times for both screw speeds represent measured time-of-first-appearance for a carbon-black tracer in the unfilled propylene. All blends were strand pelletized in line with the extruder.

Variable speed DC motors drove both primary and secondary feeders. The primary feeder was dedicated to PP and was located at the front most inlet port to the screw. The secondary feeder was used for all rubber particles and introduced this material into the melt stream through a second port located at the midpoint of the screw. A third port located approximately 200 mm on center from the die was left open for venting. Both feeders were calibrated by measuring the output versus feeder setting.

5.3.3 Specimen Molding

Compression molding was performed using a heated press (Carver, Model C) from a sandwich mold with a middle frame made from a 2 mm thick aluminum sheet. Rubber/plastic blends prepared by batch processing were placed between the platens, which were preheated to 225^{o}C. The blend was preheated for two minutes and then gradually compressed to a piston pressure of 30 MPa for an additional three minutes. Molded sheets were cooled to room temperature under a piston pressure of 100 MPa using a Schrader cooling press. The sheet was then removed and die-cut for the appropriate tests.

Injection molding of materials blended in the twin-screw extruder was performed on a 77kN electric toggle injection-molding machine (Cincinnati Milicron: Electra VE 85-5) according to ASTM D638 to provide tensile test specimens. Specimens were molded at injection velocity of 64 mm/s. Processing conditions were determined using the short shot method.

5.3.4 Characterization and Properties Testing

Apparent viscosities η were measured with a capillary rheometer (Kayeness, Galaxy IV) at 200°C. A die with an L/D ratio of 10/1 was used in all cases. Each flow curve was generated from data collected at nine different shear rates ranging from 10 to 5000 s^{-1}. Data were reduced using a two-parameter power law equation

$$\eta = k\left|\frac{\dot{\gamma}}{\dot{\gamma}_o}\right|^{n-1} \tag{4}$$

where k is the consistency index, n is the power law exponent, and $\dot{\gamma}$ and $\dot{\gamma}_o$ represent the shear rate and a reference shear rate of 1 s^{-1}, respectively.

Tensile specimens from compression-molded sheets were prepared using a specially machined half scale ASTM D638 Die D, those from injection molding were tested as molded using a Die A specimen geometry. Tensile testing was performed on an Instron 6025 with attached computer operating system and a crosshead speed of 50 mm/min. Strain was determined from the change in effective gauge length by optical methods.

Materials at various stages of processing were microtomed for optical image analysis. The image analysis system was comprised of a Micromaster stereomicroscope, a Polaroid Digital Microscope Camera, and a Gateway Performance Computer with Pentium III processor running Image J/1.18 software.

5.4 Results And Discussion

Figure 33 summarizes the experimental pathways pursued for each of the processing approaches considered. The purpose of this outline is to show the sequence of processing/characterization/testing steps and illustrate differences in how the various blends were handled that might effect experimental interpretation. Beginning with the raw polymers, the internal batch mixer provided blends in nominal quantities of 60 g. This can be contrasted with the continuous, twin-screw extruder operations that produced approximately 200 kg. Rheological testing was conducted immediately after blending. Identical flow curves were generated for each blend/processing combination. The next step was to mold the tensile test specimens. A single sheet was compression molded for each batch mixer blend and specimens prepared by die cutting. Specimens obtained from injection molding of the blends were molded directly into the desired geometry. Image analysis, utilizing the smooth molded surfaces, was used to characterize the blend's morphology. Finally, tensile test were conducted at equal crosshead speeds with the batch blends using half-scale specimens because of limited material availability.

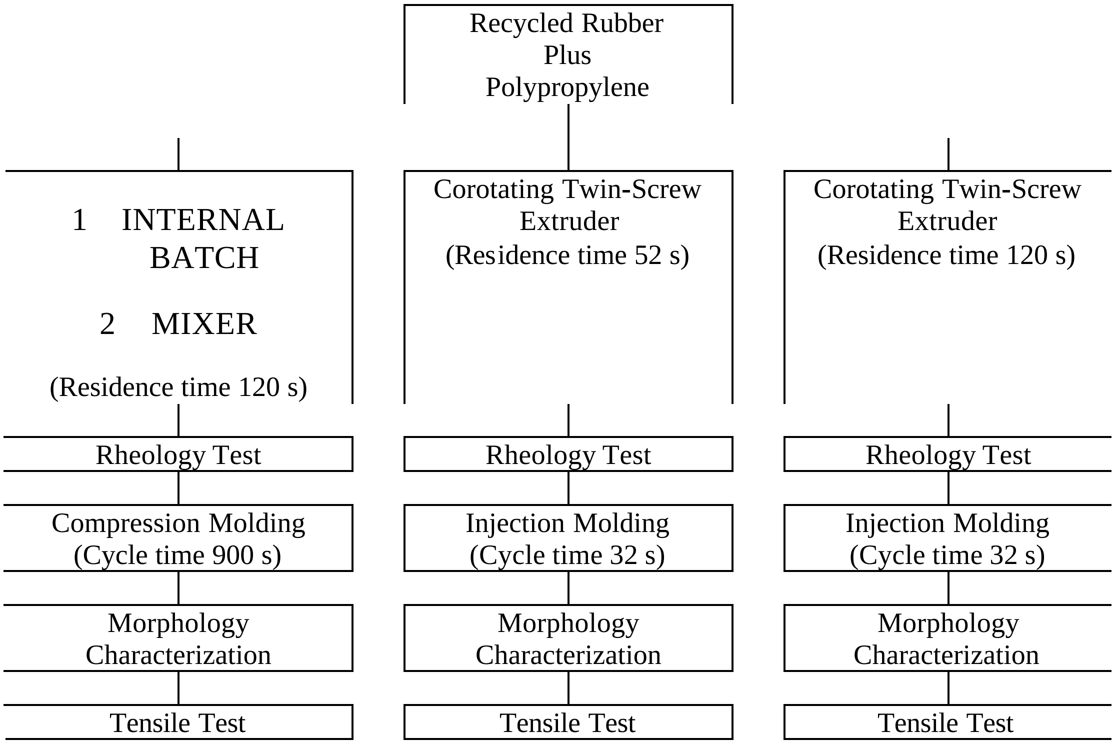


Figure 33. Experimental pathways showing order of processing/testing/characterization steps for each processing approach.

5.4.1 Rheological Testing

Illustrative flow curves for the EPDM80/PP simple blends containing 20 percent recycled rubber are shown in Figure 34. Strong pseudoplastic behavior was observed in all cases. Similar data were collected for all 18 simple blends/processing approaches considered. Data were reduced using Equation (4). Resultant power law exponents *n* and consistency indices *k* are plotted as functions of rubber content in Figure 35 to illustrate distinct behaviors within the EPDM80 blends [Figure 35(A)] and their corresponding NR/SBR versions [Figure 35(B)].

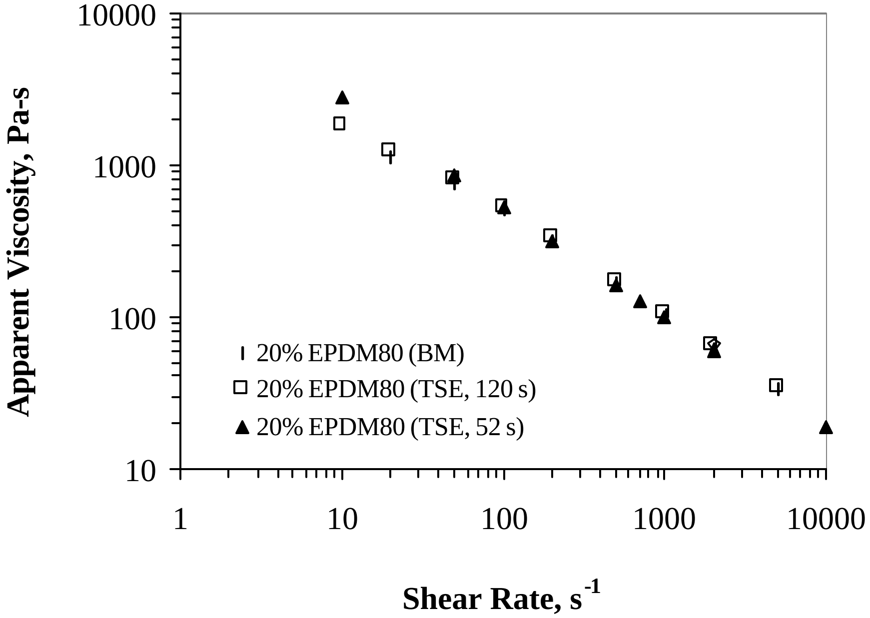
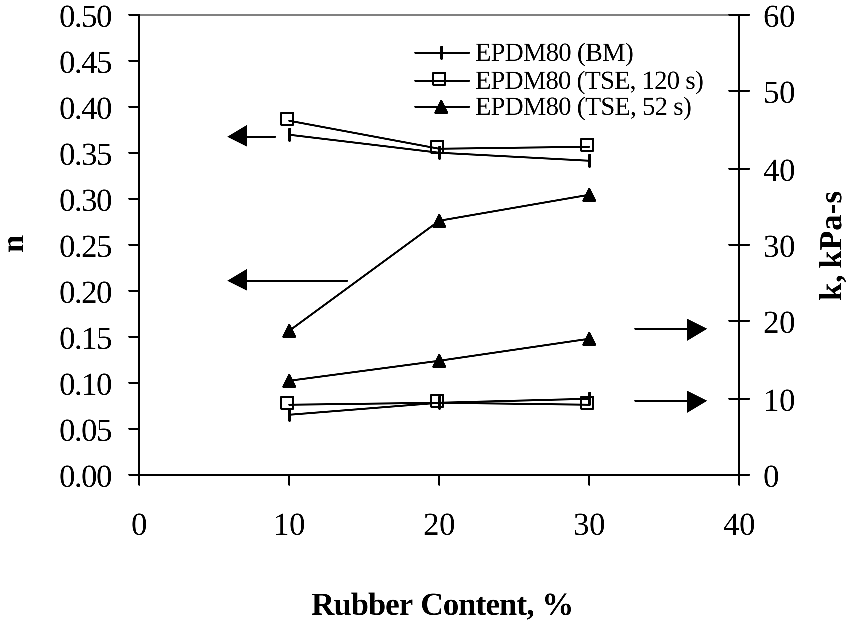


Figure 34. Flow curves for three EPDM80/PP blends containing 20 percent recycled rubber with processing condition as indicated.

Trends apparent in Figure 35 appear almost identical regardless of whether recycled EPDM80 or NR/SBR is used. Processing conditions do, however, play an important role. This is especially true for the blends prepared by twin-screw extruder with a residence time of 52 s. As previously noted, this processing approach was developed by following the manufacturers general processing guide. Figure 35 shows this approach results in a different blend as evident from lower *n* values and higher *k* values in all cases. Such behavior indicates poorer mixing under these conditions and was the reason the 120 s residence-time processing approach was developed. In addition to the longer residence time, this processing approach was also expected to generate materials with a greater resistance to flow due to the lower operating temperature. This feature could be expected to increase the shear stress experienced by the blend. Previous studies[7,8] on similar EPDM/PP blends found that polypropylene serves as the continuous phase over rubber concentrations ranging from 10 to 80 percent. This suggests that phase inversion does not play a role in interpreting the data in Figure 35.

(A)



(B)

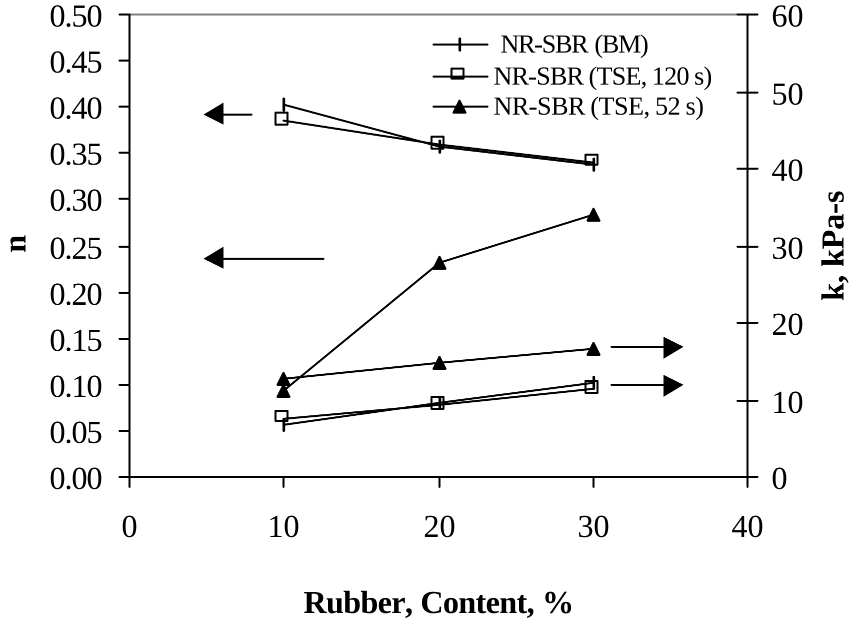


Figure 35. Reduced power law exponents and consistency indices as functions of rubber fraction for 18 simple blends/processing approaches as indicated.

Nearly identical flow responses are observed once the twin-screw extruder operating conditions were modified to more closely approximate the time/temperature/shear stress history of the batch mixer. For these two blend/processing combinations, *n* decreases, while *k* increases as more rubber is added to the blend. The increase in *k* with crosslinked rubber content is consistent the general theory for the rheology of suspensions, where resistance to flow of a composite increases exponentially with content of the dispersed phase. In this case, the carbon black filled, crosslinked elastomer acted as the dispersed solid while the PP melt served as the continuous phase. Nielsen and Landel[28] point out that hundreds of equations have been proposed to model this type of behavior dependent on the nature of the interaction between the two phases. For these blends, the viscosity rise is not as pronounced as would be expected from a rigid, solid filler, a feature that is believed attributable to the previously mentioned deformable nature of the rubber particles.

Figures 36 and 37 present identically treated rheological data for two additional families of blend/processing approaches. The first [Figure 36] shows the effect of higher rubber concentrations using the EPDM80/PP blend. In this case, rubber fraction ranges from 40 to 50 percent, and can be compared with data in Figure 37. Again, the response of the blends prepared by internal batch mixer are inconsistent with those processed in the twin-screw extruder with 52 s residence time. Figure 36 highlights the effect of rubber particle size on the rheological behavior of EPDM/PP blends. These materials were processed using the 170 mesh, or smaller particle size EPDM, and can also be directly compared with those previously discussed in Figure 35. Rubber particle size, at least at these concentrations and for these sizes, appears to have little or no impact on these rheological properties. A 120 s residence time twin-screw extruder run was not accomplished on either of the blend families shown in Figures 36 or 37.

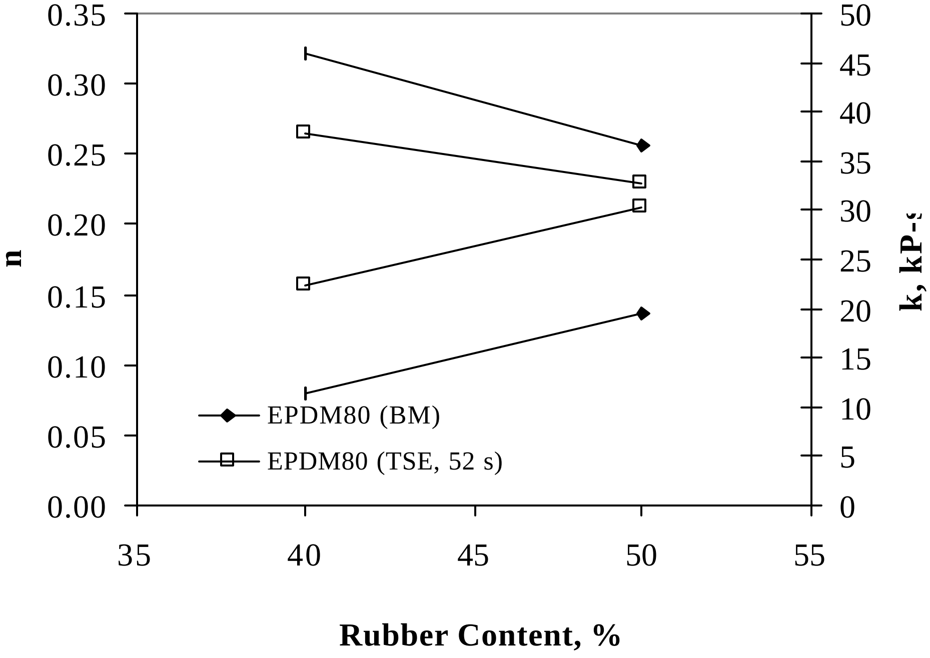


Figure 36. Reduced power law exponents and consistency indices as functions of rubber fraction for four reactive EPDM80 blends/processing approaches.

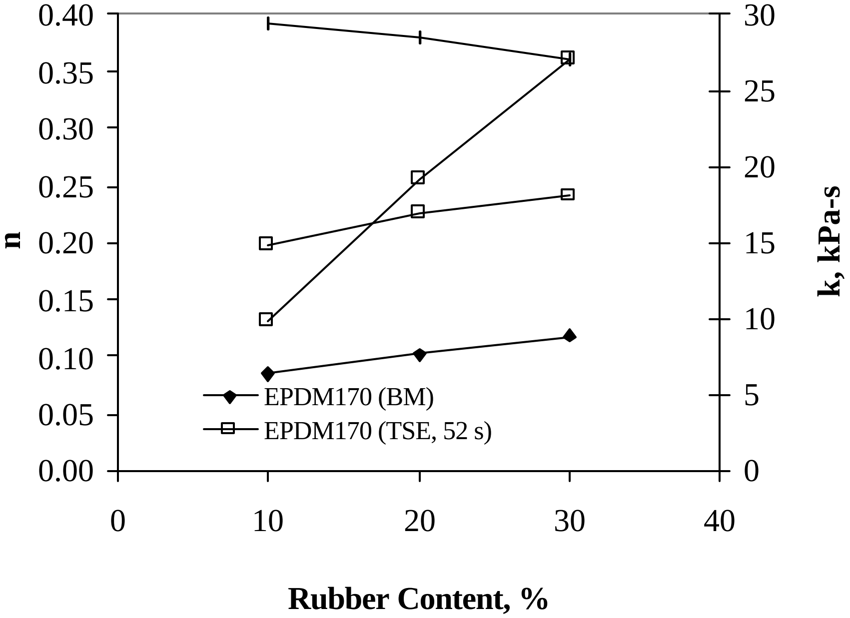


Figure 37. Reduced power law exponents and consistency indices as functions of rubber fraction for six EPDM170 blends/ processing approaches as indicated

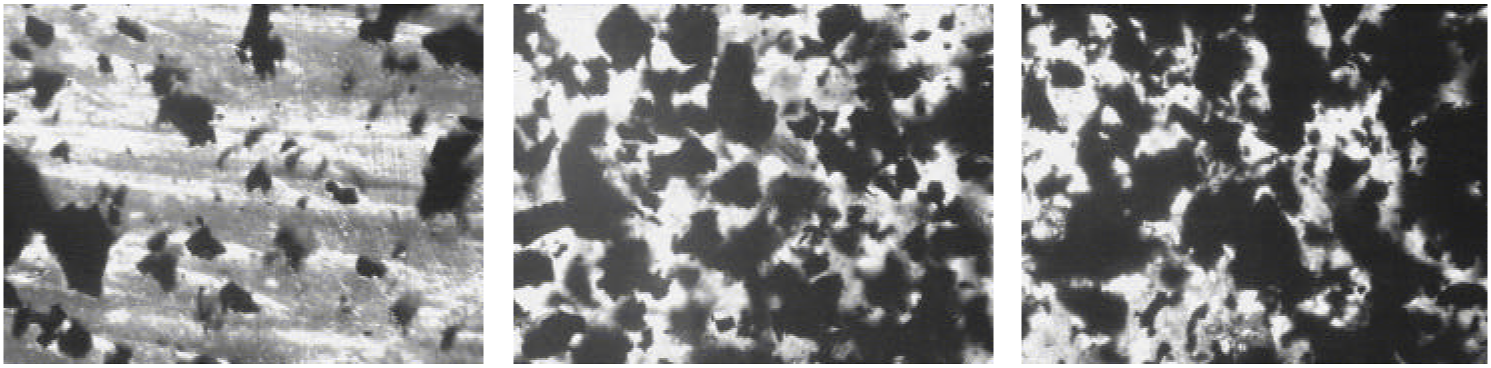
5.4.2 Morphological Characterization

Image analysis was conducted to evaluate differences in the mixing morphology between blends prepared by internal batch mixing versus twin-screw extrusion at equivalent (as determined from capillary rheometer data) processing conditions. Figure 38 presents photomicrographs obtained from NR/SBR simple blends processed using each approach. Visual inspection indicates that the rubber particles are better dispersed by batch mixing at the10 and 20 percent concentrations. The superior degree of dispersion is less clear at 30 percent.

More information concerning the efficacy of mixing can be obtained if the intensity of segregation is considered. The intensity of segregation is a measure of the degree-of-mixedness. It is defined as[29,30]

$$I = s^2/\mathbf{s}_o^2 \qquad (5)$$

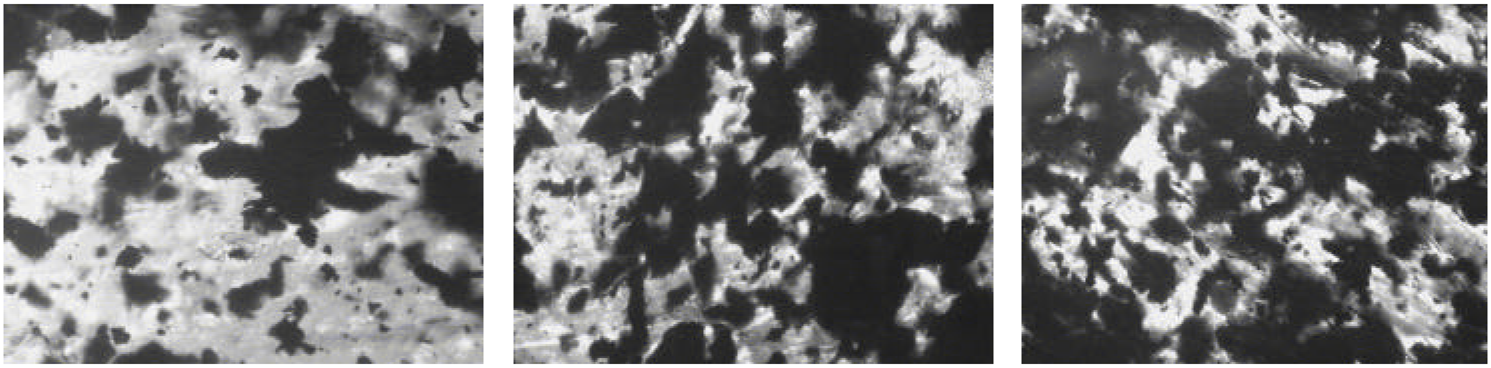
where s^2 is the variance of actual concentration from its mean value and $\mathbf{s}_o^2$ is the theoretical variance of a completely segregated mixture, or totally unmixed system. As I approaches zero the mixture is considered homogeneous, and is fully segregated near the other extreme of unity. Intensity measurements corresponding to the micrographs in Figure 37 are 0.022, 0.037, and 0.056 for the batch mixed blend, and 0.077, 0.046, and 0.048 for blend prepared by twin-screw extrusion, at rubber concentrations of 10, 20, and 30 percent, respectively. These are consistent with the visual observations previously discussed and suggest that at low rubber concentrations, the internal batch mixer is superior. As rubber content increases, the two mixing approaches converge.



10% NR-SBR
Batch Mixing
(Residence Time = 2 min)

20% NR-SBR
Batch Mixing
(Residence Time = 2 min)

30% NR-SBR
Batch Mixing
(Residence Time = 2 min)



10% NR-SBR
Twin Screw Compounding
(Residence Time = 2 min)

20% NR-SBR
Twin Screw Compounding
(Residence Time = 2 min)

30% NR-SBR
Twin Screw Compounding
(Residence Time = 2 min)

Figure 38. Photomicrographs of simple NR/SBR/PP blends with indicated rubber content and processing method. (Width of each micrograph's field of view is 500 mm.)

5.4.3 Tensile Testing Results

Mechanical properties for the 18 simple blends/processing approaches are considered in Figures 39 and 40. In general, tensile stress capability decreases almost linearly with increasing rubber content. These data are consistent with a volume rule of additivity whereby the higher strength polypropylene material is gradually diluted by a fractionally added lower strength recycled elastomer. Strength data range from a high near 25 MPa to a low just below 15 MPa for the NR/SBR blends, while their EPDM counterparts only reach a high of approximately 20 MPa. For the NR/SBR blends, ordering with respect to strength indicates batch mixing provides the best properties, followed closely by the 120 s residence time twin-screw extrusion. The material blended by the 52 s approach displayed the weakest breaking stress capabilities. A less distinct trend is noted for the EPDM blends, where a crossover in all three curves complicates an ordering with respect to strength.

Correspondingly, the tensile strain data generally increases with rubber fraction. This increase is relatively small and not as distinct for the NR/SBR blends, with all the observed elongational capabilities within the 20 to 50 percent range. Of the three processing approaches considered, twin-screw extrusion with the 120 s residence time provides the highest values, while the internal batch mixer displays the lowest. More dramatic effects are noted for the EPDM blends. Again, the twin-screw extruder with the 120 s residence time is superior with values ranging from near 100 to near 300 percent for 10 and 30 percent EPDM powder, respectively. Internal batch mixing produces the least elongational capability, ranging from approximately 50 to near 150 percent for corresponding rubber fractions.

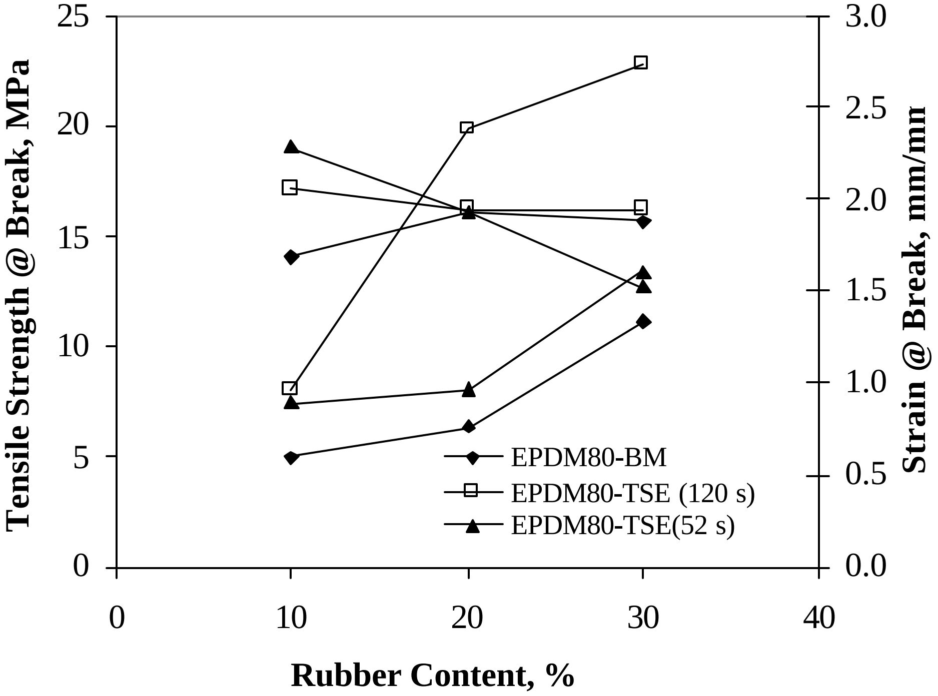


Figure 39. Mechanical properties of simple blends with blend components and processing approaches as indicated.

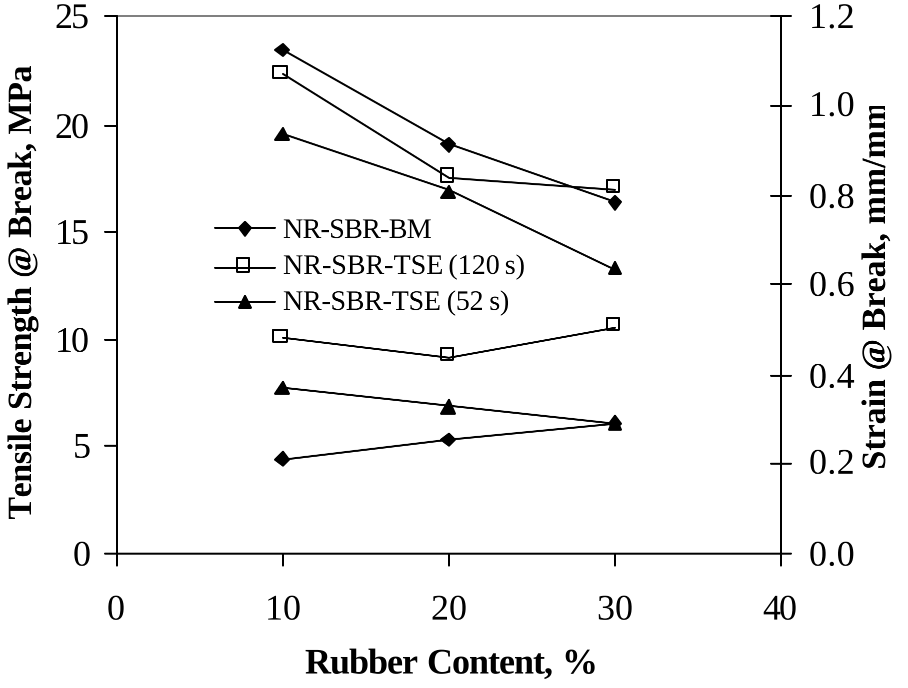


Figure 40. Mechanical properties of simple blends with blend components and processing approaches as indicated.

The mechanical properties of the two additional blend families, whose rheological properties were discussed previously, are shown in Figures 41 and 42. Figure 41 presents the EPDM80/PP blends extended to rubber concentrations of 40 and 50 percent. These represent continuations of the trends noted previously with the twin-screw extruder closely approximates the stress capabilities of the blends prepared by internal batch mixing. The primary difference is seen here again as a higher elongation at break for those blends processed via twin-screw extrusion. Finally, data for the mechanical failure of rubber/plastic blends utilizing EPDM170 are given in Figure 42. These show that the smaller particle size provides greater strain capabilities for blends processed in the internal batch mixer, but no concomitant change in stress capability. As previously noted, scale-up to twin-screw extrusion at the slower rate was not accomplished on these last two families of blends.

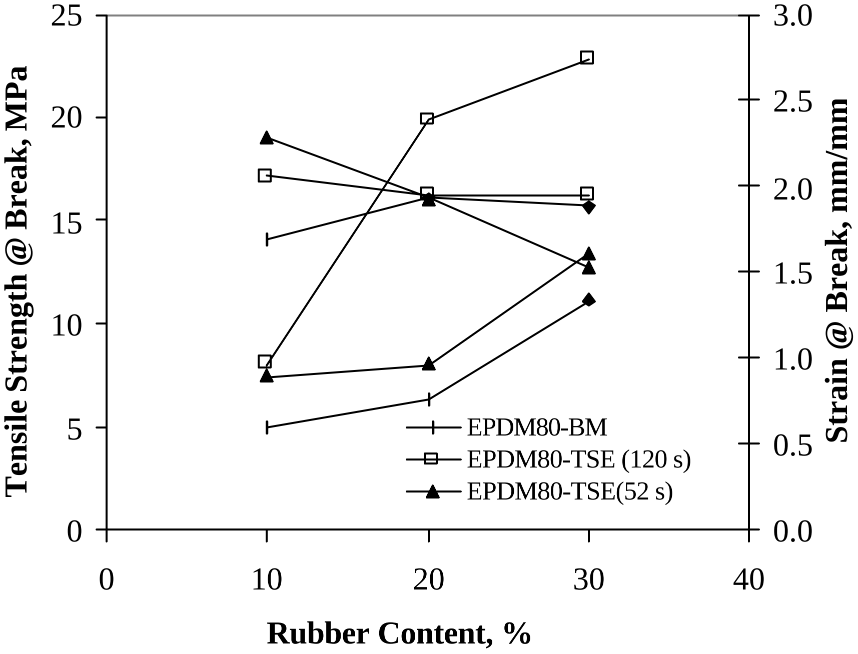


Figure 41. Mechanical properties of simple blends with blend components and processing approaches as indicated.

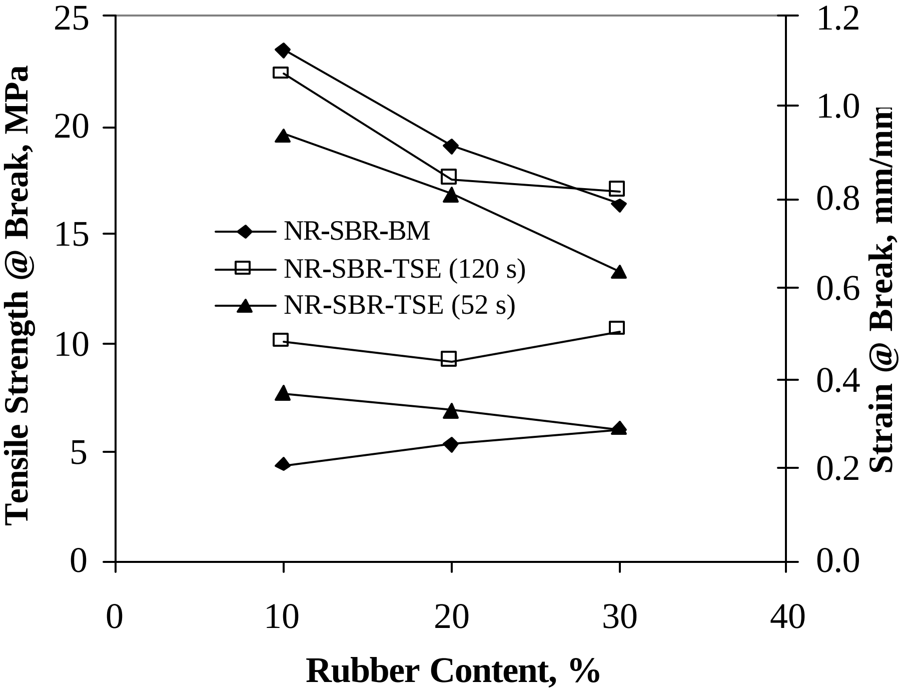


Figure 42. Mechanical properties of simple blends with blend components and processing approaches as indicated.

5.5 Conclusions

An experimental investigation has been conducted to scale-up a series of recycled rubber/polypropylene blends developed for internal batch mixing. Scale-up was accomplished using an intermeshing, corotating twin-screw extruder. It was found that if the processing conditions are modified in an attempt to mimic parameters of the batch mixer, blends with similar rheological and mechanical properties can be produced. Image analysis revealed that even though agreement is excellent with respect to physical properties, the internal mixer still provides a superior degree of dispersion as quantified in the paper by the intensity of segregation.

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6 CONCLUSIONS

There are many problems associated with the disposal of both scrap tires and other rubber products. Scrap tire landfills occupy precious land, while scrap tire piles act as fire hazards and breeding grounds for mosquitoes and diseases that they can carry. This work has looked at methods to recycle ground scrap rubber into new and useful materials. Specifically, this work investigated blends of thermoplastics with recycled ground rubber. The recycled ground rubber was blended with PP to form a new material that can be used in applications such as sports surfaces. In addition, this new material is easily recycled simply by heating. In essence, the work has converted a thermoset material into a thermoplastic, which can be reused and converted into new products simply by re-heating the material and forming it into shape in much the same manner as other thermoplastics.

A variety of blends were prepared to determine the effect of rubber particle size, MFI of the PP, weight percent rubber, and type of thermoplastic on the physical properties of the blends. In addition, several blend compatibilization techniques were developed. Design of experiments reveals that the most crucial factor to produce a composite with appreciable improvement in the mechanical properties is the melt flow index, indicating that the molecular structure of the thermoplastics plays a critical role in the blending. Rubber particle size and residence time play less, nevertheless very important, role in the blending. The rheological tests reveal that the blends are more sensitive to shear at a higher rubber contents.

Studies of the simple blending of scrap rubber and thermoplastics reveals that a composite with improved tensile properties can be achieved by adopting suitable thermoplastics. An elongation of more than 800% was achieved in the composite of EPDM rubber and ethylene octene copolymer. However, simple blending techniques are not applicable for most compositions, where rubber with PP gives poor mechanical properties. Compatibilization techniques were successfully developed to overcome this limitation.

Three chemical compatibilizing techniques were discovered to create new thermoplastic/recycled rubber blends. For EPDM rubber and polypropylene, a radical initiated compatibilization approach was employed leading to dramatic improvements in the blend properties. For SBR and polypropylene, a phenolic process was employed with preformed phenolic resin as the grafting agent. The third compatibilizing technique takes advantage of the styrene in the SBR rubber. By using Lewis acid catalyst, polypropylene chain was grafted on to the SBR rubber through so-called Friedel-Crafts reaction.

It was found that the radical initiated compatibilization greatly improved the EPDM/PP composite, and new TPEs with similar and better tensile properties than that of commercial TPEs were produced. Less improvement was obtained in the case of phenolic and Friedel-Crafts compatibilization.

The determinative factor to scale up the blending is the residence time. A comparison of batch mixer and twin-screw extruder was studied and it was concluded that a composite of similar mechanical properties was obtained provided that the average residence time is the same as that of batch mixer.

7 ACKNOWLEDGEMENTS

The authors wish to acknowledge support during the conduct of this study from the Chelsea (Massachusetts) Center for Recycling and Economic Development for funding the study. We would also like to express gratitude to Dow Chemical,Huntsman, Montell Polyolefins Erickson Rubber, Fina Oil and Chemical, and Rouse Rubber for supplying materials.