

Effect of Grafted Maleic Anhydride Content and Recyclability of Dynamically Cured Maleated Natural Rubber/Polypropylene Blends

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ABSTRACT: Maleated natural rubbers (MNRs) were prepared using various levels of maleic anhydride (MA) at 4, 6, 8, 10, and 12 phr. Dynamically cured 60/40 MNR/PP blends with phenolic-modified polypropylene (Ph-PP) compatibilizer at a loading level of 5 wt % of PP were prepared by melt mixing process using sulfur vulcanization system. The influence of the level of MA on properties of the thermoplastic vulcanizates (TPVs) was studied. It was found that the mixing torque, apparent shear stress, shear viscosity, tensile strength, and hardness properties increased with increasing levels of the MA or grafted succinic anhydride groups in the MNR molecules. This is attributed to an increase in chemical interaction and reaction between methylol groups in the Ph-PP molecules and polar functional groups in the MNR molecules upon increasing levels of the

grafted succinic anhydride groups. As a consequence, compatibilizing block copolymers of MNR and PP blocks were formed. The block copolymers were capable of compatibilizing with MNR and PP blend components via the respective blocks. Recyclability of the MNR/PP TPVs was also studied. It was found that, after processing through a number of cycles by injection molding and extrusion processing, the TPV exhibited marginal decreases in mechanical properties. This corresponded to slightly increasing size of the dispersed vulcanized rubber domains. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 4071–4078, 2008

Key words: maleated natural rubber (MNR); polypropylene; anhydride; rheological; mechanical; morphological properties; recyclability

INTRODUCTION

Thermoplastic vulcanizate (TPV) or dynamic vulcanizate (DV) is a class of thermoplastic elastomers (TPEs) based on rubber and thermoplastic compositions where the rubber phase is dynamically vulcanized. The TPVs are characterized by finely dispersed micron-sized crosslinked rubber particles distributed in a thermoplastic matrix.¹ The DVs show their advantages over traditional thermoplastic elastomer. That is, the TPVs exhibited higher elastomeric properties because they contain vulcanized rubber domains dispersed in thermoplastic phase. They also exhibit superior aging and weathering resistance because the rubber domains surrounded with the continuous thermoplastic matrix. Most polyolefin TPEs are based on synthetic rubbers such as ethylene-propylene-diene monomer (EPDM), ethylene

propylene rubber (EPR), and butadiene acrylonitrile rubber (NBR) or a modification of them. Thermoplastic elastomer based on natural rubber and thermoplastic blend, classically meets the definition of thermoplastic natural rubbers (TPNRs). Not only raw NR has been used to prepare TPNRs but also modified forms have been widely studied. Epoxidized natural rubber (ENR) is one of the most recognized forms. It has been used to prepare TPNRs by blending with various thermoplastics such as polypropylene,^{2–5} poly(vinyl chloride),^{6,7} poly(ethylene-co-acrylic acid),⁸ and poly(methyl methacrylate).^{9,10} Graft copolymer of NR with PMMA has also been used to prepare TPNRs.^{11–14} In recent years, attempts were made to prepare TPNRs based on maleated natural rubber (MNR) and PP blends via dynamic vulcanization process. The effect of blend ratios on rheological, mechanical, and morphological properties of the MNR/PP TPVs was investigated.¹⁵ A simple blend (i.e., a blend without curatives) of MNR and polypropylene using phenolic-modified polypropylene (Ph-PP) and polypropylene-g-maleic anhydride (PP-g-MA) compatibilizers was also reported.¹⁶ Furthermore, rheological, thermal, and morphological properties of reactive blending based on MNR and PMMA have also been described.¹⁷

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TABLE I
Compounding Formulation

Ingredients	Quantities (parts by weight)
MNR ^a	100
ZnO	6.0
Stearic acid	0.5
Wingstay L	1.0
TBBS	1.0
Sulfur	3.5

^a Various types of MNRs (i.e., MNR-4, MNR-6, MNR-8, MNR-10, and MNR-12).

In this work, TPNRs based on 60/40 MNR/PP TPVs with Ph-PP compatibilizer were prepared via dynamic vulcanization process. The influence of the level of MA used in preparation of the MNR on rheological, mechanical, and morphological properties of the TPVs was investigated. Furthermore, recyclability for this type of TPV was also studied.

EXPERIMENTAL

Materials

Polypropylene used as a thermoplastic blend component was an injection-molding grade MD with MFI of 12 g/10 min at 230°C and specific gravity of 0.91, manufactured by the Thai Polypropylene, Rayong, Thailand. The natural rubber used was air-dried sheet (ADS), manufactured by a local factory operated by Khun Pan Tae Farmer Co-operation (Phattalung, Thailand). The MA used to prepare the graft copolymer of MA and natural rubber or MNR was manufactured by Riedel-de Haen, Seelze, Germany. The toluene used as a solvent was manufactured by Lab Scan, Ireland. The zinc oxide and stearic acid used as activators in the sulfur vulcanization system were manufactured by Global Chemical, Samutprakarn, Thailand and Imperial Chemical, Pathumthani, Thailand, respectively. The sulfur used as a vulcanizing agent was manufactured by Ajax Chemical, Samutprakarn, Thailand. The *N-tert-butyl-2-benzothiazolesulphenamide* (Santocure TBBS) used as an accelerator was manufactured by Flexsys (USA). The polyphenolic additive, Wingstay (L, used as an anti-oxidant was manufactured by Eliokem (Ohio).

Preparation of MNR and Ph-PP compatibilizer

MNR and Ph-PP were prepared by melt mixing process in an internal mixer, Brabender Plasticorder PLE 331 (Duisberg Germany) using preparation and characterization techniques according to our previous work.¹⁶ In the case of MNR, the melt blending of ADS with MA with five concentrations of MA at 4, 6, 8, 10, and 12 phr was performed. The MNR products were later named as MNR-4, MNR-6,

TABLE II
Mixing Schedule of Rubber Compounding

Descriptions	Mixing time (min)
Rubber mastication	5
Stearic acid	1
ZnO	1
Wingstay L	1
TBBS ^a	2
Sulfur	2
Compound finishing	3

^a *N-tert-butyl-2-benzothiazolesulphenamide*.

MNR-8, MNR-10, and MNR-12, respectively. The Ph-PP was also prepared via melt blending process of phenolic resin (SP-1045) with PP in a presence of Lewis acid ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), as described elsewhere.^{4,16}

Preparation of dynamically cured 60/40 MNR/PP TPVs

The MNRs were first compounded using a two-roll mill at a room temperature as for the compounding formulation and mixing schedule shown in Tables I and II, respectively. The 60/40 MNR/PP TPVs were then prepared via dynamic vulcanization during melt mixing using a Brabender Plasticorder at 180°C, and a mixing schedule as shown in Table III. This blend ratio was selected because the TPV with superior in rheological and mechanical properties with the smallest dispersed vulcanized rubber domains dispersed in the PP matrix was observed.¹⁵ The PP was first preheated for 6 min in the mixing chamber without rotation. It was then melted for 2 min at a rotor speed of 60 rpm. The Ph-PP compatibilizer at a loading level of 5 wt %¹⁶ was incorporated and mixed for 1 min. The MNR compound was added and mixing was continued until a plateau mixing torque was reached. The blend products were finally pelletized. MNRs with five levels of MA used in the graft copolymerization (i.e., MA = 4, 6, 8, 10, and 12 phr) were each studied. Mechanical, rheological, and morphological properties of the TPVs were later characterized.

Recycling of MNR/PP TPVs

The TPV prepared based on MNR with 8 phr of MA (i.e., MNR-8) was selected to test for recyclability.

TABLE III
Mixing Schedule for Preparation of Dynamically Cured MNR/PP/TPVs in an Internal

Descriptions	Mixing time (min)
Warming of PP	6
Melting of PP	2
Add compatibilizer (Ph-PP)	1
Add MNR compound	Until plateau mixing torque

The experimental procedure was based on a conventional injection molding process where the test specimens were fabricated using an injection nozzle temperature of 180°C. Mechanical and morphological properties of each reprocessing cycle were determined. After the tests, the product was reground and pelletized by extrusion with a die temperature of 180°C. The other three different zones along the barrel of the injection molding machine and extruder were set using the same temperature, at 160, 170, and 180°C, respectively. A series of three alternations of injection molding and extrusion were performed. Mechanical and morphological properties of the recycled material were documented and compared with the virgin material results.

Rheological characterization

A Rosand single bore capillary rheometer (model RH7, Rosand Precision, Gloucestershire, UK) was used to characterize shear flow properties in terms of relationship between apparent shear stress and shear viscosity with apparent shear rate. The test was carried out at a wide range of shear rates (50–1600 s⁻¹) at a test temperature of 180°C. Dimensions of the capillary die used were 2 mm diameter, 32 mm length, and 90° entry angle with the aspect ratio (L/D) of 16/1. The material was first preheated in a rheometer's barrel for 5 min under a pressure of ~ 3–5 MPa to get a compact mass. The excess molten material was then automatically purged until no bubbles were observed. The test was then carried out at a series of shear rates set in a program via a microprocessor. During the test, the pressure drop across a capillary channel and melt temperature was captured via a data acquisition system. The apparent values of shear stress, shear rate, and shear viscosity were calculated using derivation of the Poiseuille's law for capillary flow.¹⁸

Mechanical testing

Tensile testing of the samples was performed at 25°C ± 2°C at a crosshead speed of 500 mm/min according to ISO37. The instrument used was a Hounsfield Tensometer, model H 10 KS manufactured by the Hounsfield Test Equipment, UK. The dumbbell-shaped specimens, 2 mm thick, were prepared by a thermoplastic injection molding machine with a capacity of clamping force of 90 tons (Welltec Machinery), Hong Kong. Hardness of the samples was also measured using indentation shore A, according to ISO 7619.

Morphological studies

Morphological studies were carried out using a Leo scanning electron microscope, model VP 1450, man-

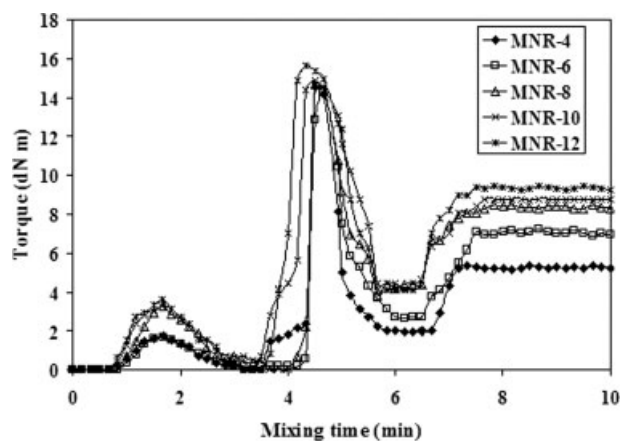


Figure 1 Torque-time curves of dynamically cured 60/40 MNR/PP TPVs with five types of MNRs.

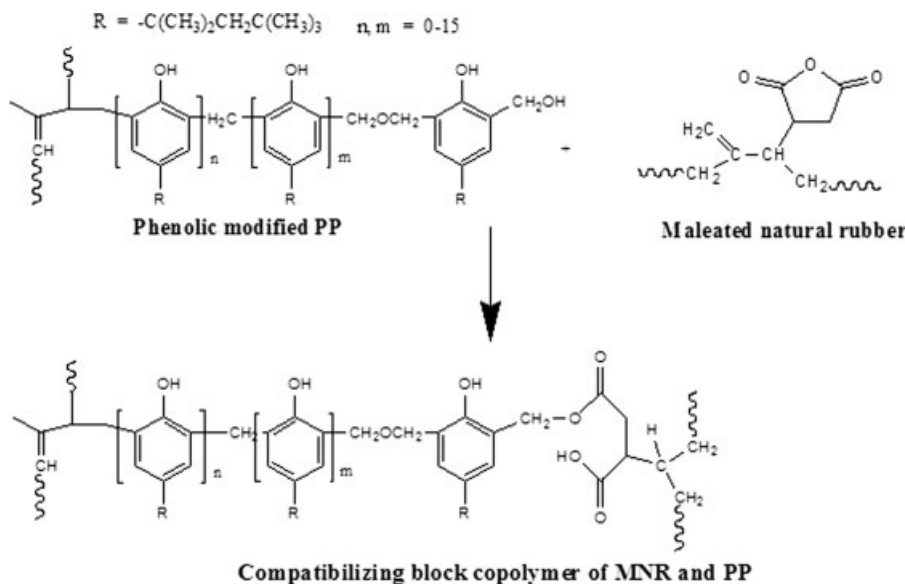
ufactured by Leo, Cambridge, UK. Molded samples of the TPVs were cryogenically cracked in liquid nitrogen to avoid any possibility of phase deformation. The PP phase was extracted by immersing the fractured surface into hot xylene for 10 min. The samples were later dried in a vacuum oven at 40°C for 3 h. The dried surfaces were later gold-coated and examined by scanning electron microscope.

RESULTS AND DISCUSSION

Influence of MA content

Mixing torque

Figure 1 shows the mixing torque-time curves of the dynamically cured 60/40 MNR/PP TPVs using MNRs with various levels of MA used in the graft copolymerization. It can be seen that the mixing torque rose sharply after the rotors were started because of the resistance exerted on the rotors by the unmelted PP. The torque then decreased because the PP melted on account of mechanical shearing and heat transfer from the heater. This created the first group of peaks of the mixing torque-time curves. A second group of higher peaks was observed after incorporation of MNR compounds. The mixing torque again sharply rose and created a second peak because of resistance of the unmelted material. The torque was thereafter reduced because of melting of the MNR compound. The mixing torque finally rose again because of dynamically cured MNR phase. The plateau mixing torque-time curves were observed after a mixing time of ~ 7 min and 30 s. The mixing was continued until a total mixing time of ~ 10 min. This was to ensure fully vulcanized rubber phase. It can be seen that the height of the second peak and final mixing torque increased with increasing levels of MA used in the graft copolymerization. That is, the height of the second



Scheme 1 Possible reaction between Ph-PP and MNR to form compatibilizing block copolymer of PP and MNR.

and final mixing torque can be ordered according to the concentration of MA used in the graft copolymerization as follows: MA = 12 (MNR-12) > MA = 10 (MNR-10) > MA = 8 (MNR-8) > MA = 6 (MNR-6) > MA = 4 (MNR-4). This may be attributed to an increasing trend of chemical interaction between MNR molecules as well as between MNR and PP phases at increasing concentrations of MA. Increasing quantities of MA in the graft copolymerization caused an increasing trend of the grafted succinic anhydride groups in the MNR molecules. That is, the MNRs prepared using concentrations of MA at 4, 6, 8, 10, and 12 phr gave the grafted succinic anhydride groups at 2.69, 3.55, 4.16, 5.26, and 7.14 wt %, respectively.¹⁷ As a consequence, the interfacial forces between vulcanized domains of MNRs and PP phase were increased because of higher capability of the Ph-PP compatibilizer to combine the MNR molecules via the polar functional groups. This leads to a formation of the compatibilizing block copolymers of PP and MNR, as a proposed reaction mechanism shown in Scheme 1. The compatibilizing block copolymers are capable of interaction with the blend components by the respective blocks.

Rheological properties

Plots of apparent shear stress versus shear rate (i.e., flow curves) and apparent shear viscosity versus shear rate (i.e., viscosity curves) of dynamically cured 60/40 MNR/PP TPVs using various types of MNRs are shown in Figures 2 and 3, respectively. It can be seen that the flow and viscosity curves of the TPVs increased with an increase in MA content in the graft copolymerization. Trends of the flow and

viscosity curves corresponded to the trends of final mixing torque (Fig. 1). This is attributed to higher chemical interaction between the rubber and PP phase via the compatibilizing effect of Ph-PP.

Mechanical properties

Effects of various types of MNRs on tensile strength and hardness properties of TPVs prepared from dynamically cured 60/40 MNR/PP blends are shown in Figure 4. It can be seen that the tensile strength and hardness increased with an increasing concentration of MA in the graft copolymerization.

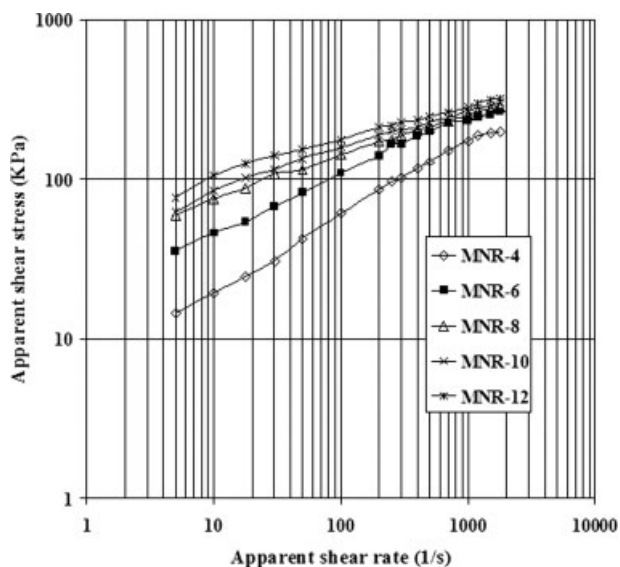


Figure 2 Relationship between apparent shear stress and shear rate of dynamically cured 60/40 MNR/PP TPVs with five types of MNRs.

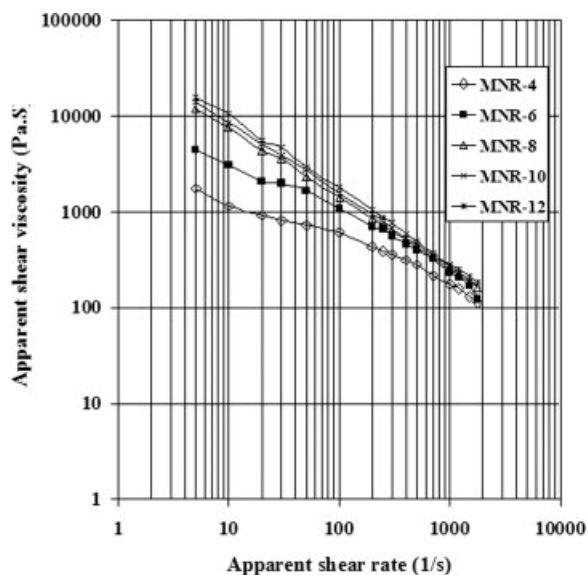


Figure 3 Relationship between apparent shear viscosity and shear rate of dynamically cured 60/40 MNR/PP TPVs with five types of MNRS.

This might be attributed to an increase in interfacial force between the interface of PP and MNR phases with increasing level of the grafted succinic anhydride groups in the MNR molecules. Therefore, the polar functional groups in the Ph-PP molecules (i.e., $-\text{CH}_2\text{OH}$) increased their capability to interact with the polar functional groups in the MNR molecules with higher grafted succinic anhydride groups. The PP blocks in the compatibilizing block copolymers (Scheme 1) are also capable of compatibilizing with the PP blend component. Furthermore, the MNR vulcanizates, with higher grafted succinic anhydride groups, are stronger because of higher chemical interaction within and between MNR molecules via the polar functional groups. As a consequence, a formation of permanent covalent and hydrogen bonds might form within in an intermolecular manner.

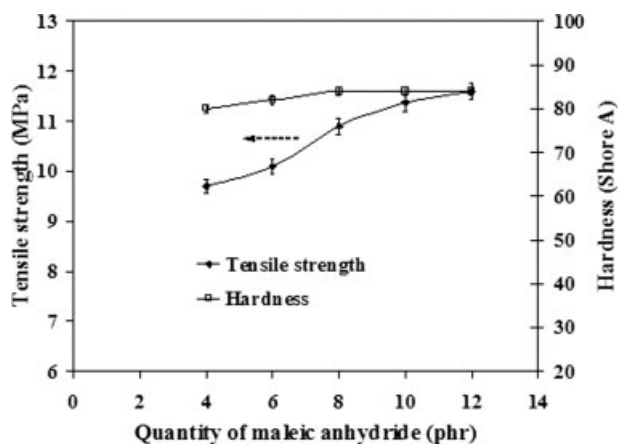


Figure 4 Tensile and hardness of dynamically cured 60/40 MNR/PP TPVs with five types of MNRS.

This could lead to the formation of harder and more rigid material, as the increasing trend of tensile strength and hardness properties suggests (Fig. 4).

Figure 5 shows elongation at break and tension set of the dynamically cured 60/40 MNR/PP TPVs using various types of MNRS. A decreasing trend of the elongation at break but increasing trend of tension set with increasing levels of MA were observed. This is attributed to increasing rigidity of the MNR molecules at increasing levels of the grafted succinic anhydride groups. This leads to lower extensibility and a tendency to snap-back after a prolonged extension of the TPVs. It is also seen that all TPV specimens exhibited tension set lower than 20% and elongation at break greater than 250%. This reveals that these types of TPVs exhibited good elastomeric properties.

Morphological studies

The solvent-etched cryogenic fractured surfaces of the 60/40 MNR/PP TPVs with five types of MNRS are shown in Figure 6. Xylene was used to extract the PP phase at high temperature. That is, the thermoplastic phase was dissolved in hot xylene, which left spherical vulcanized rubber particles adhered at the surfaces. The previous location of the PP phase was changed to a cavitation. The two-phase morphology for these types of dynamically cured TPVs was confirmed, according to the TPVs main characteristic. Also, the micron size spherical domains of the dispersed vulcanized MNR phase in the PP matrix were clearly observed. It is also seen that sizes of dispersed vulcanized rubber domains decreased with an increase in levels of grafted succinic anhydride groups in the MNR molecules. That is, the TPVs with MNR prepared with MA at 4, 6, 8, 10,

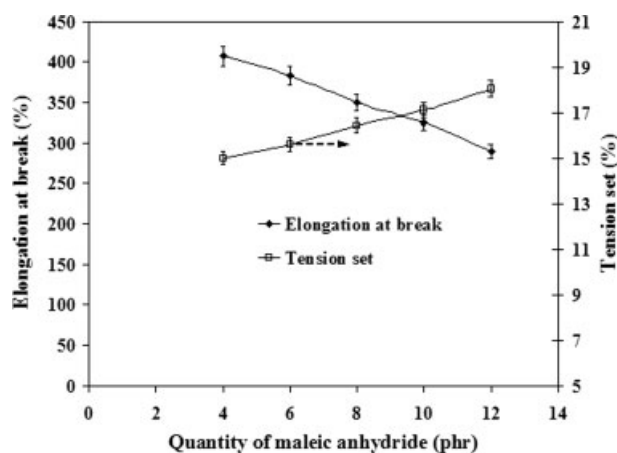


Figure 5 Elongation at break and tension set of dynamically cured 60/40 MNR/PP TPVs with five types of MNRS.

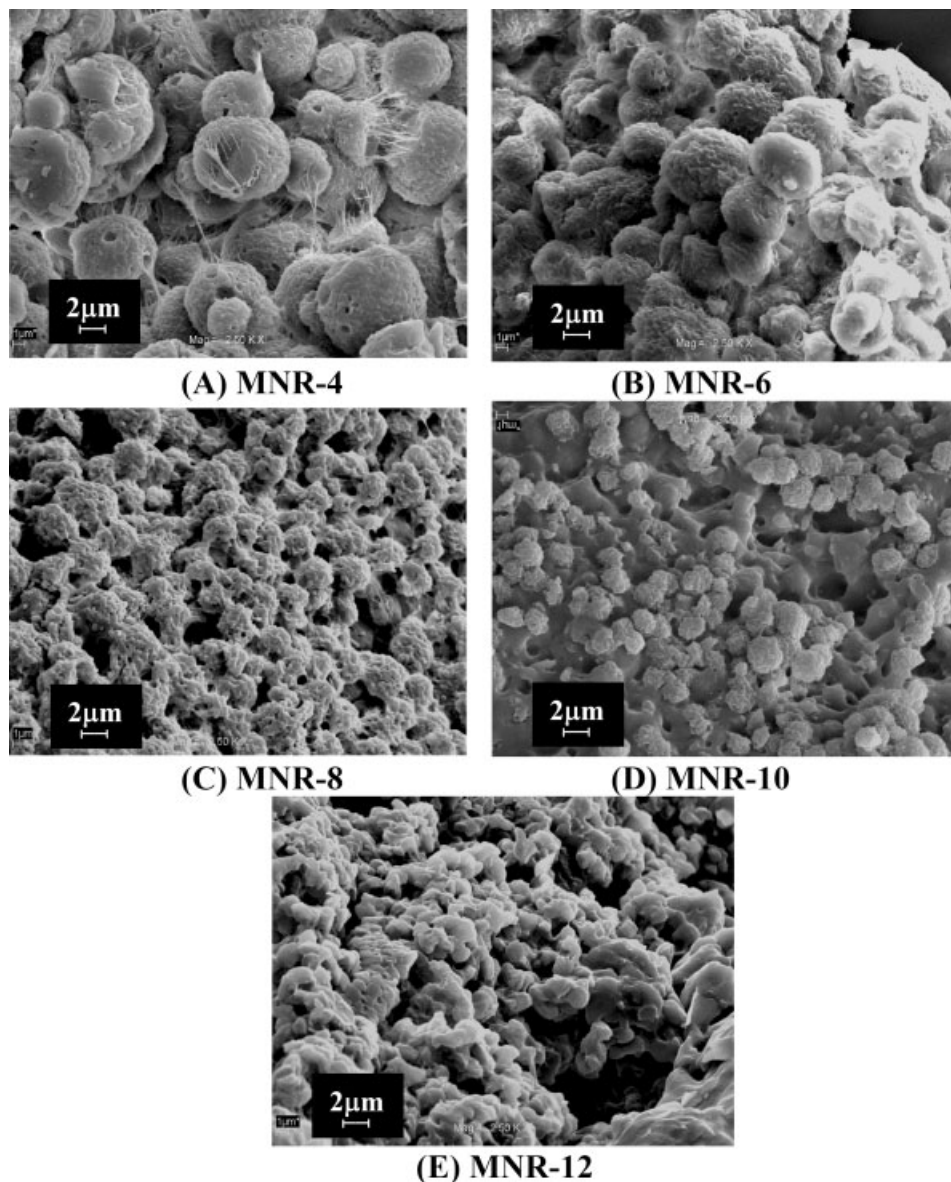


Figure 6 SEM micrographs of dynamically cured 60/40 MNR/PP TPVs with five types of MNRs.

and 12 phr exhibited the average particle sizes ~ 4 , 2, 1, 0.8, and $0.5 \mu\text{m}$, respectively. Increasing trend of polarity of the rubber phase caused higher chemical interaction between MNR and PP phases via the compatibilizing block copolymer of the Ph-PP. Consequently, higher interfacial adhesion between MNR and PP phases was obtained. This caused decreasing sizes of vulcanized rubber domains with increasing level of the grafted succinic anhydride groups. As a consequence, higher interfacial adhesion force and hence higher strength and hardness properties (Fig. 4) of the TPVs with higher levels of the grafted succinic anhydride groups. Also, higher mixing torque, flow curves, and viscosity curves (Figs. 1–3, respectively) were observed in the TPVs with higher concentrations of MA in the graft copolymerization.

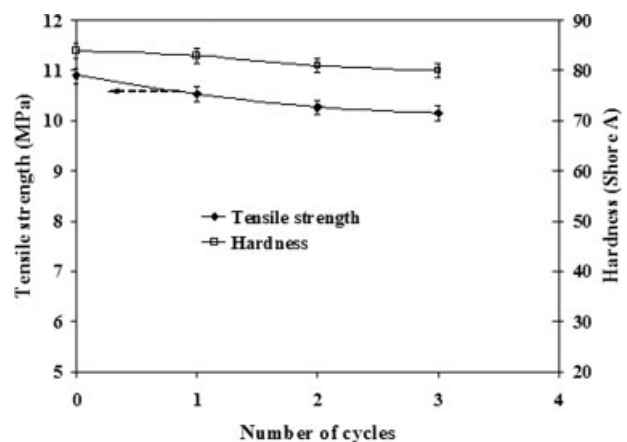


Figure 7 Tensile strength and hardness of recycled 60/40 MNR-8/PP TPVs compared with virgin material.

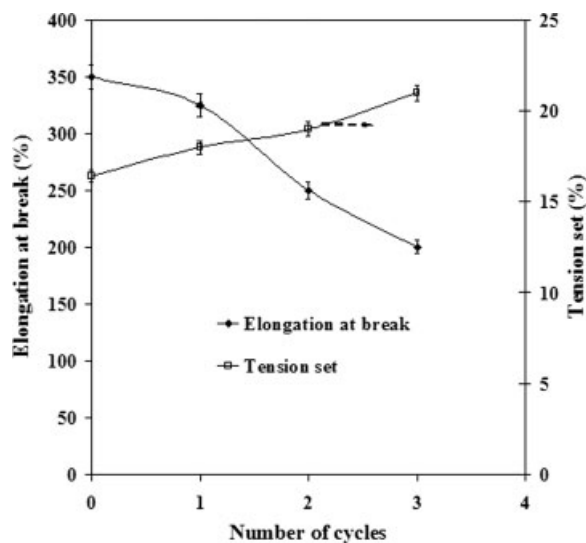


Figure 8 Elongation at break and tension set of recycled 60/40 MNR-8/PP TPVs compared with virgin material.

Recyclability of dynamically cured MNR-8/PP TPVs

Figure 7 shows tensile strength and hardness of recycled MNR/PP TPVs compared with the virgin material. It is seen that the strength and hardness properties were marginally decreased with increasing number of reprocess cycles. However, in

Figure 8, a slight decreasing trend of elongation at break and tendency to recover to the original shape after extension (i.e., increasing trend of tension set) were observed. This is attributed to degradation of the PP and vulcanized rubber phases. It has been well established that PP degrades under a cycle of heat treatments, and hence decreases in its molecular weight,^{19,20} viscosity, and mechanical strength.²⁰ According to the SEM results (Fig. 9), it is clear that larger cavitations were observed where the PP phase was previously located. This might be a result of degradation of PP molecules, and hence a lowering of its melt viscosity during injection molding and extrusion processes. Hence, the vulcanized rubber domains were capable of coalescing to form larger particles and also create larger occupied volume by the PP phase, as shown in Figure 9. The vulcanized rubber was also capable of degrading under the repeated high heat and shearing force conditions. However, the vulcanized rubber domains are always in an unmelted state. Therefore, the degradation at the surface of the particles might be more pronounced. This also causes the tendency to coalescence in the rubber particles. As a result, decreasing interfacial force between the phases, and hence lowering of the mechanical strength and elastomeric properties in terms of elongation and set properties were observed. However, various properties of the

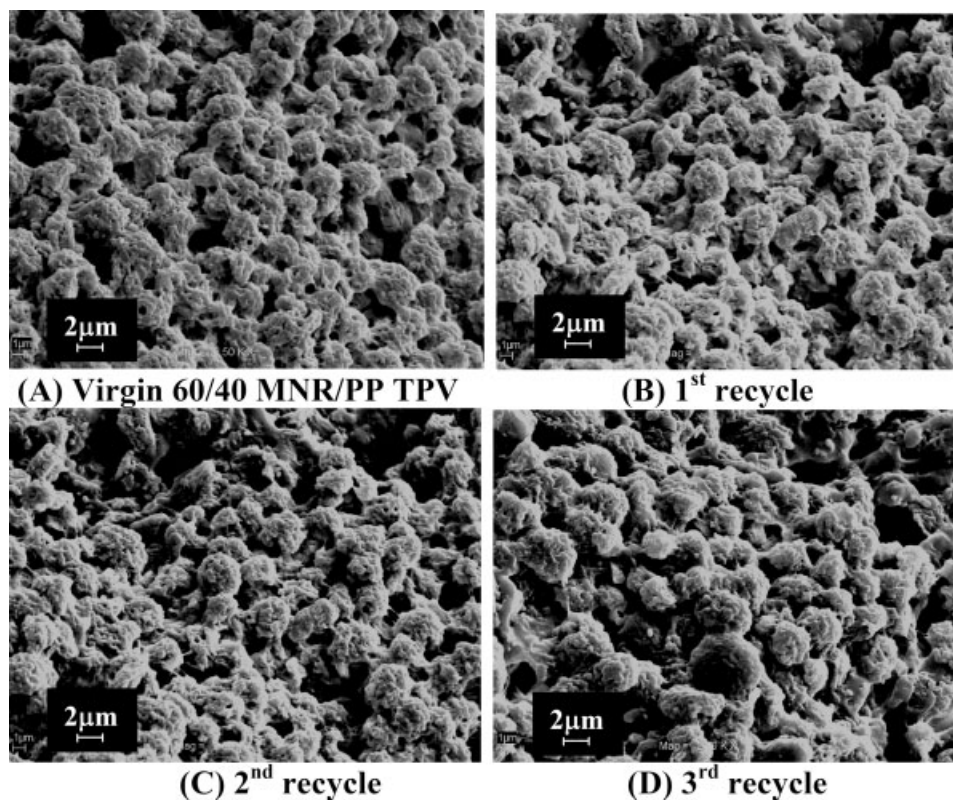


Figure 9 SEM micrographs of recycled 60/40 MNR-8/PP TPVs compared with virgin material.

TPV from a final recycling process were more or less in a range of capability to apply in some industrial applications. That is, the tensile strength, elongation at break, and tension set are ~ 10 MPa, 200, and 21%, respectively. It is therefore concluded that MNR/PP TPV is recyclable. It still retains useful properties even after experiencing high shear and heat treatment from a number of recycling process.

CONCLUSIONS

The dynamically cured 60/40 MNR/PP TPVs with Ph-PP compatibilizer were prepared by a melt mixing process via dynamic vulcanization using a sulfur vulcanization system. Influence of level of grafted succinic anhydride groups in the MNR molecules or levels of MA used in the graft copolymerization on properties of the TPVs was studied. It was found that the mixing torques, flow curves, viscosity curves, tensile strength, and hardness properties increased with an increase in levels of MA used in the graft copolymerization. This is attributed to an increase in chemical interaction between methylol groups in the Ph-PP molecules and polar functional groups in the MNR molecules upon increasing levels of MA. This caused a formation of compatibilizing block copolymers of PP and MNR. Also, the PP blocks in the Ph-PP molecules are capable of compatibilizing with the PP molecules in the blend composition. Higher interaction also caused smaller sizes of the dispersed vulcanized rubber domains. A decreasing trend of resistance to permanent set and elongation at break was also observed with increasing level of the grafted succinic groups in the MNR molecules. This is attributed to increasing interaction and hence rigidity of the vulcanized MNR phase with higher succinic anhydride contents. The MNR-

8/PP TPVs were reprocessed through a number of cycles of injection molding and extrusion. It was found that after three cycles, the TPV still retained useful mechanical strength and elastomeric properties.

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