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Original Article

The effect of the ratios of sulfur to peroxide in mixed vulcanization systems on the properties of dynamic vulcanized natural rubber and polypropylene blends

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Abstract

This study investigated the influence of various ratios of sulfur to peroxide during vulcanization on the rheological properties, morphology and crystallinity of natural rubber/polypropylene thermoplastic vulcanizates (TPVs) blended at a fixed ratio of 60/40. The results show that the addition of peroxide into the mixed vulcanization system has an important effect on the properties of the TPVs as a result of two competing reactions which occur simultaneously in the natural rubber (NR) and the polypropylene (PP) phases. These are cross-link reactions of NR molecules with different cross-link patterns, cross-link density being caused by the proportions of sulfur and peroxide curing agents and the degradation of the PP through β-chain scission. This causes significant variations in the phase morphology of the TPVs and the crystallization of the PP. Further, different trends of changes in properties were observed according to the peroxide content in the mixed vulcanization system. This study found that a ratio of 70/30 parts of sulfur to peroxide provided a better overall balance of properties of the NR/PP TPVs than those of TPVs produced using sulfur or peroxide alone or other ratios of mixed sulfur/peroxide vulcanization systems.

Keywords: polymer blends, curing of polymers, rheological properties, morphology, crystallization

1. Introduction

The development of polymer blends has been widely studied for many decades, driven mainly by enhancements in their properties. Thermoplastic vulcanizates (TPVs) are a type of polymer blend prepared by the high shear blending of *in-situ* dynamic cross-linked elastomer with molten thermoplastic (Coran, 1987; Karger-Kocsis, 1999). This dynamic vulcanization improves the phase morphology of TPVs from the co-continuous phase morphology of a simple blend without cross-linking agents into micron sized finely dispersed cross-linked elastomer particles in a continuous thermoplastic matrix (De and Bhowmick, 1990). The size of the elastomer particles depends on the compatibility of the blend components and the melt viscosity of the blend. It has been reported that the viscosity of TPVs changes according to the vulcanization system and increases based on the cross-link concentration (Akhtar *et al.*, 1987; Nakason *et al.*, 2008). Since the type of cross-linking agent is an important factor affecting the melt viscosity and properties of TPVs, many cross-linking systems have been applied to dynamically vulcanize the elastomer phase (Akiba and Hasnim, 1997; Maiti *et al.*, 2006). The most commonly used cross-linking systems are the sulfur vulcanization system (Sombatsompop *et al.*, 2007; Ghosh *et al.*, 1996), the peroxide system (Thitithammawong *et al.*, 2009; Babu *et al.*, 2009) and phenolic resin (Tanrattanakul *et al.*, 2009; Pichaiyut *et al.*, 2008).

Recently, a mixture of the sulfur and peroxide systems has been employed to vulcanize the rubber phase in TPVs (George *et al.*, 1999; Nakason *et al.*, 2006a; Nakason *et al.*, 2006b) because this combines the cross-link patterns of the $-S_x-$ linkages from sulfur based agents and the –C-C- linkages

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from peroxide. This significantly improves the properties of TPVs by reducing permanent set, improving elastic recovery, mechanical properties and high temperature utility, and promoting resistance to attachment by fluids. The stability in the phase morphology falls between those of pure sulfur and pure peroxide systems (Nakason *et al.*, 2006a; Nakason *et al.*, 2006b).

Even when very low concentrations of peroxide are used in a combined sulfur/peroxide vulcanization system, close attention needs to be paid to TPVs with a polyolefin thermoplastic matrix in general and especially those with polypropylene (PP). The free radicals generated from peroxide not only cause a cross-link reaction in the elastomer phase but also promote a competitive β-chain scission reaction in the PP molecules by the abstraction of a tertiary hydrogen atom from the main chain. Both of these reactions are significant with regard to the properties of TPVs.

Many studies (Li *et al.*, 2009; Babu *et al.*, 2008; Thitithammawong *et al.*, 2007a; Thitithammawong *et al.*, 2007b; Naskar, 2007; Naskar and Noordermeer, 2003) have reported on the effect of peroxide concentrations in the curing system on the properties of TPVs with PP as the thermoplastic matrix. The balance of the cross-link reaction and the chain scission has been found important. Appropriate vulcanization of the rubber molecules and chain scission of the PP in the TPVs can improve the mechanical, dynamic mechanical, rheological, and morphological properties. On the other hand, degradation of PP has been observed (Chatterjee and Naskar, 2007; Azizi and Ghasemi, 2004) at a high content of peroxide, combined with a decrease in the mechanical properties of the TPVs. The quantity of peroxide in the cross-linking agent is a factor that directly affects the final properties of the TPVs. However, most studies have fixed the contents of the two cross-linker components and compared the results with using sulfur or peroxide individually. The effect of the ratio of sulfur and peroxide on the mechanical and thermal properties of the TPVs produced was recently reported by Thitithammawong *et al.* (2012)

The main objective of the present work is to study the effects of different ratios of sulfur to peroxide in a mixed sulfur/peroxide vulcanization system at a fixed blend ratio of natural rubber and PP. The study has also been broadened to consider the effect of the vulcanization reaction from the mixed cross-linking agents in combination with the competitive peroxide reactions, and how these competing reactions influence the rheological properties of TPV, the crystallizing tendency of PP, and the morphological evolution of the blend components.

2. Experimental

2.1 Materials

The RSS3 natural rubber (NR) was obtained from Khuan Pun Tae Farmer Co-operation, Phattalung, Thailand. The polypropylene (PP) was PP700J, with a melt flow index (MFI) of 11.5g/10 min and a specific gravity of 0.90, and was manufactured by the Thai Polypropylene Co., Ltd. (Rayong, Thailand). The dicumyl peroxide (DCP) used as a curing agent was manufactured by Wouzhou International Co., Ltd., China. Ultrasil VN 3 Gr silica filler was supplied by Siamsilica Co., Ltd., Thailand. The co-agent, trimethylolpropane trimethacrylate (TMPTMA) and the silane coupling agent, bis-{3-triethoxy-silyl}-propyl}-tetrasulfide (or Couplink 89) were manufactured by Behn Meyer Chemical Co., Ltd. A PP-g-PhHRJ compatibilizer was prepared in-house according to a procedure described elsewhere (Thitithammawong *et al.*, 2008). PP (100 parts by weight) was first mixed in an internal mixer with four parts by weight of dimethyol phenolic resin (PhHRJ) for three minutes. Stanous dichloride at 0.8 parts by weight was later added, and mixing was continued for two minutes. The product was cooled to room temperature and ground into small pieces with a Bosco plastic grinder. Before being used as a compatibilizer, the product was purified by extraction with acetone. Other chemicals used for the sulfur vulcanization were of commercial grade and were used in the state received.

2.2 Mixing and preparation of the NR/PP thermoplastic vulcanizates

Pre-compounded NR was first prepared by blending the NR with the chemicals shown in Table 1, on a two-roll mill at room temperature for 35 minutes. The pre-compounded rubber was then sheeted out and kept at room temperature for one day before being used. The 60/40 NR/PP TPVs were prepared by melt-mixing in an internal mixer (Model MX500-D75L90, Chareon Tut, Co., Ltd., Samut Prakan, Thailand) at 170 °C and at a constant rotor speed of 60 rpm. The PP was first put into the mixing chamber and mixed for five minutes before adding the PP-g-PhHRJ compatibilizer. Mixing continued for two minutes before the Ultra-plast-TP01 plasticizer was fed into the mixture for one minute. Finally, the pre-compounded NR was introduced into the chamber and the mixing continued for another seven minutes to complete the dynamic vulcanization process. The TPV produced was immediately removed from the chamber and was later fabricated into dumbbell-shaped specimens using an injection-molding technique with a clamping force of 90 tons (Weltec Machinery, Ltd., Hongkong, China).

In this study, the effects of various ratios of sulfur to peroxide in the mixed sulfur/peroxide vulcanization system were investigated. As a reference, TPVs were also prepared by using 100% sulfur or peroxide cross-linking agents. The compound formulations of the NR/PP TPVs are shown in Table 2.

2.3 Rheological characterizations

The rheological properties of the TPVs were established using a rotorless oscillating shear rheometer (RheoTech MDPT, Cuyahoya Falls, USA) at 170°C. The oscil-

Table 1. Compounded NR composition in parts per hundred parts of rubber (phr) with varying proportions of sulfur/peroxide

Chemicals	Quantities (phr)						
	100/0	90/10	70/30	50/50	30/70	10/90	0/100
RSS 3	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Wingstay L (Antioxidant)	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Napthenic oil	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Silica	30.0	30.0	30.0	30.0	30.0	30.0	30.0
DEG	1.8	1.8	1.8	1.8	1.8	1.8	1.8
Couplink 89 (Silane)	1.8	1.8	1.8	1.8	1.8	1.8	1.8
Sulfur	2.0	1.8	1.4	1.0	0.6	0.2	-
MBTS	1.0	0.9	0.7	0.5	0.3	0.1	-
DCP	-	0.1	0.3	0.5	0.7	0.9	1.0
TMPTMA	-	0.2	0.6	1.0	1.4	1.8	2.0

Table 2. Composition of NR/PP TPVs and mixing time

Chemicals	Quantities (part)	Mixing time (min)
PP	40.0	5
PP-g-PhHRJ compatibilizer (7% w/w of PP)	2.8	2
Ultra-plast-TP01 processing aid (5% w/w of NR)	3.0	1
NR Compound (part of NR without chemicals)	60.0	Until plateau mixing torque

lation frequency was set in the range of 1–15 Hz at a constant strain of 3%. This was to ensure that the test was located in the linear viscoelastic region. The storage modulus (G2), loss factor tan $\delta = G''/G'$ and the complex viscosity $\eta^* = 3G^*/\omega = \eta'' + i\eta'$ of the TPVs were established.

2.4 Morphological analysis

A scanning electron microscope (SEM, model VP 1450, Leo Co., Ltd., Cambridge, U. K.) was used to conduct morphological analysis of the NR/PP TPVs. The injection-molded samples were cryogenically fractured in liquid nitrogen to prevent any possibility of phase deformation during the fracture process. The PP phase was preferentially extracted by immersing the fractured surface into xylene at 110°C for 30 minutes. The samples were dried in a vacuum oven at 40°C for 24 hrs to eliminate the solvent, and gold-coated before their characteristics were established using a SEM.

2.5 X-ray diffraction studies

An X-ray diffractometer (XRD, Philips® TW1830, Amelo, The Netherlands) operating at 15 kV, and 5 mA with Cu Kα radiation monochromatized with a graphite sample monochromator ($\lambda = 1.54$ Å) was used to establish the crystallinity characteristics. The diffractograms were scanned in a 2θ range of 10-25° at a rate of 0.5°/min. The degree of crystallinity of the NR/PP TPVs was quantitatively estimated by calculating their relative peak intensity following Guan *et al.* (2003). A smooth curve connected with the peak baseline was computer-plotted based on the diffraction measured. It was noted that some of the points did not lie on the smooth curve. The area above the smooth curve, A_c was interpreted as representing the crystalline portion, while the lower area between the smooth curve and the linear baseline connecting the two points of intensity at 2θ of 10-25°, A_a was taken to represent the amorphous portion. The upper and lower areas were used to determine the crystallinity as follows:

$$X_C = \left(\frac{A_C}{A_C + A_a} \right) \times 100 \quad (1)$$

The relative amount of the β phase, K_β in the crystalline portion of the material was calculated according to equation 2 (Guan *et al.*, 2003):

$$K_\beta = \frac{I_{300}^{\beta}}{I_{110}^{\alpha} + I_{040}^{\alpha} + I_{130}^{\alpha} + I_{300}^{\beta}} \quad (2)$$

where I^{β}_{300} is the integral intensity of 300 reflections of the β phase and $I^{\alpha}_{110,}$ $I^{\alpha}_{040,}$ and I^{α}_{130} are the integral intensities of the 110, 040, and 130 reflections of the α–phase, respectively. Finally, using Bragg's equation, the interplanar spacing (d) between the diffracting planes in the PP crystalline structure was calculated as follows:

$$\mathrm{d} = \frac{\mathrm{n}\lambda}{2\sin\theta} \quad (3)$$

where n (an integer) is the order of reflection, λ is the wavelength of the incident X-rays used (1.54 nm), and θ is the scattering angle of incidence.

2.6 Differential scanning calorimetry measurements

Differential scanning calorimetry (DSC) measurements were carried out using a differential scanning calorimeter (Perkin Elmer® DSC7, Norwalk, CT) in the temperature range of 50°C to 200°C at a heating rate of 10°C/min under nitrogen atmosphere. The samples underwent a series of scans: (a) first heating, followed by (b) cooling, and then (c) second heating at the same rate of 10 °C/min. The degree of crystallinity of the PP was determined from the heating curve by using the following formula:

$$X_i = \left(\frac{\Delta H_{TPVs}}{m_{PP} \cdot \Delta H_{PP}} \right) \times 100 \quad (4)$$

where X_i is degree of crystallinity (%), ΔH_{TPVs} is the apparent melting enthalpy of the crystallinity of the PP (J/g), ΔH_{PP} is the extrapolated value of the melting enthalpy of the crystallization of a 100% crystalline sample; for PP the value is 209 (j/g) (Bieliñski *et al.*, 1997; Kukaleva *et al.*, 2000), and m_{PP} is the weight fraction of PP in the blend.

3. Results and Discussion

3.1 Rheological properties

Dynamic frequency sweep tests were performed at fixed low strain amplitude (in the linear viscoelastic region) using a rotorless oscillating shear rheometer. These tests aimed to study network formation and microstructural changes in the TPVs. Figure 1 to 3 show plots of the storage modulus, tan δ, and complex viscosity as a function of frequency (Hz) for the dynamically vulcanized NR/PP TPVs with various ratios of sulfur to peroxide in the mixed sulfur/peroxide vulcanization system.

It can be observed from Figure 1 and 2 that the proportions of sulfur and peroxide have a significant effect on the storage modulus and loss factor (tan δ) of the TPVs. The sulfur system displays the highest storage modulus with the

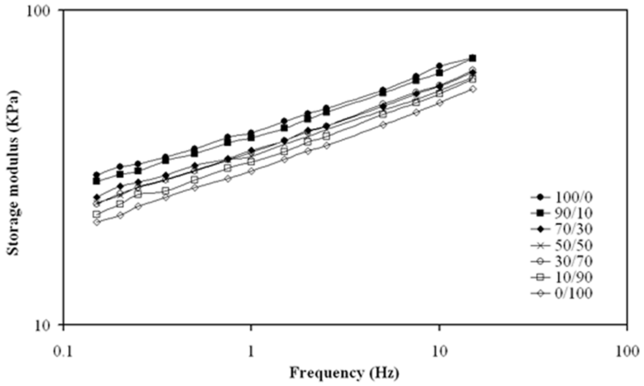

Figure 1. Storage modulus of NR/PP TPVs with various ratios of sulfur to peroxide in the mixed sulfur/peroxide vulcanization system.

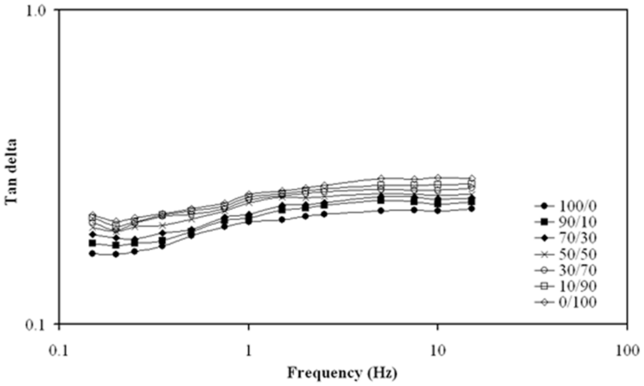

Figure 2. Tan d of NR/PP TPVs with various ratios of sulfur to peroxide in the mixed sulfur/peroxide vulcanization system.

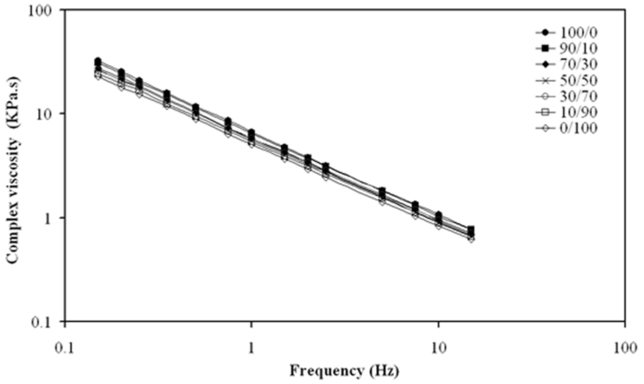

Figure 3. Complex viscosity of NR/PP TPVs with various ratios of sulfur to peroxide in the mixed sulfur/peroxide vulcanization system.

lowest tan δ, whereas the relationship of the storage modulus and tan δ resulting from the peroxide curing system are reversed. The employment of the mixed sulfur/peroxide system results in intermediate values of these two properties. It should be noted that at a testing temperature of 170°C, crystallinity in the PP was absent. The PP phase was molten, in the form of a flowing fluid. However, vulcanized NR particles still remained at this temperature since the chemical cross-linking of intermolecular chains suppressed their mobility in the NR. Therefore, the whole system behaved like a dispersion of the elastic NR filler particles dispersed in the PP matrix. The behavior of these two phases affected the rheological response of the TPVs. The findings of this study are an indication of the dispersed NR particles (i.e., amount, size and crosslink density), the properties of the PP matrix and the interaction between both phases. The change in rheological properties can be also attributed to the influence of the types of chemical bonds in the NR vulcanizates and the influence of competitive reactions in the matrix from the sulfur and peroxide during dynamic vulcanization as recently report by Thitithammawong *et al.* (2012). The sulfur system provides NR/PP TPV with sufficient cross-link density in the NR vulcanizates and no degradation of the PP takes place. Therefore, the rubber molecules respond well to the application of force due to the flexibility of the rubber chains with low damping of the molecules. As a result, the TPVs produced have good dynamic properties at testing temperature. On the other hand, with the addition of peroxide into the mixed vulcanization system, the degradation of the PP overshadows the effect of the cross-linking of the NR phase. The peroxide curing system yields TPVs with insufficient cross-linking and severe degradation of the PP. Furthermore, the possibility of the production of excess co-agents to form higher modulus filler-like domains of thermoset co-agent (Henning, 2007; Liu *et al.*, 2004) together with an interpenetrating network of homopolymerized co-agents (Yu *et al.*, 2011; Dluzneski, 2001) as illustrated in Figure 4, may result in a reduction in the extent of cross-link reaction during vulcanization. As a consequence, the NR/PP TPV exhibits poor dynamic properties with the highest damping and the lowest storage modulus. In contrast, the mixed sulfur/peroxide system yields TPVs with intermediate properties as a result of the effects of the sulfur and peroxide on the NR and PP molecules with higher proportions of peroxide resulting in competitive reactions and inferior dynamic properties in the NR/PP TPVs.

Figure 3 illustrates the complex viscosity of the NR/PP TPVs produced with different proportions of sulfur and peroxide in the vulcanization system. The complex viscosity decreases with increasing frequency (Hz) for all the TPVs, showing pseudoplastic behavior. Similar to the storage modulus, the complex viscosity decreases continuously with the proportion of peroxide. The phenomena observed in this rheological study match the expectations from a reduction in the cross-link density in the rubber phase and decreasing molecular weight of the PP in the presence of peroxide radicals. Also a decrease in melt viscosity was observed. These results are in accordance with the observations of George *et al.* (1999), Azizi and Ghasemi (2004), and Babu *et al.* (2010a, 2010b).

3.2 Morphological studies

SEM micrographs of NR/PP TPVs with various ratios of sulfur to peroxide in the mixed vulcanization system were studied. The morphologies of the cryogenic fractured surface of the samples are shown in Figure 5. The NR/PP blend vulcanized with the sulfur system has the largest particle size, while in the mixed and the peroxide vulcanization systems, the distribution is finer and more uniform than that of the sulfur vulcanization system. The size of NR particles in the vulcanized TPVs was in agreement with their rheological properties as the high degree of cross-linking of the rubber

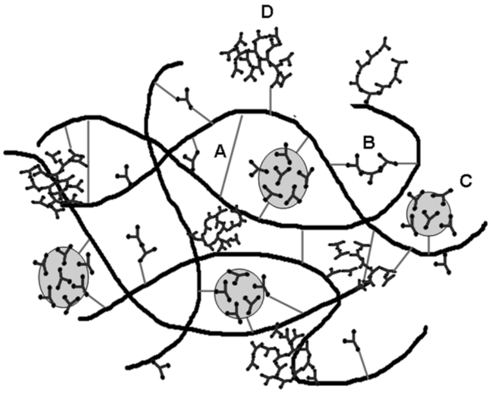

Figure 4. Idealized network derived from peroxide curing agent in presence of co-agent. Cross-links can be derived from; (A) polymer radicals, (B) co-agent forming cross-links, (C) thermoset domains of co-agent grafted to polymer chains, and (D) interpenetrating network of homopolymerized co-agents (Henning, 2007).

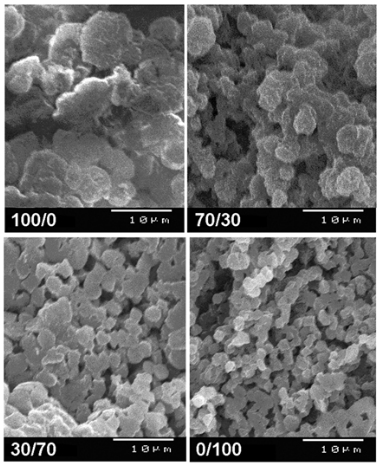

Figure 5. SEM micrographs of NR/PP TPVs with various ratios of sulfur to peroxide in the mixed sulfur/peroxide vulcanization system.

molecules provided large sized rubber domains (Nakason *et al.*, 2006a).

3.3 X-ray diffraction analysis

To understand the change in the properties in the NR/PP TPVs at different proportions of peroxide in the mixed sulfur/peroxide vulcanization system, the crystallinity level and the patterns of the PP phase were studied using the X-ray diffraction technique. Figure 6 shows X-Ray diffractograms for pure PP, NR/PP TPVs and NR vulcanizate. The diffraction pattern has a broad amorphous background on which are superimposed sharp crystalline peaks. An exception to this pattern is the diffractogram for NR vulcanizate which was obtained for the purpose of comparison and presents only the broad amorphous background with no pronounced crystalline peaks. Generally, pure PP has three crystalline structures: α-monoclinic, β-pseudohexagonal and γ-triclinic. The formation of these varied crystal modifications is dependent on the crystallization conditions. The formation of the last two crystalline structures (β-pseudohexagonal and γ-triclinic) is particularly difficult and they are unstable, unlike the a-monoclinic structure (Norton and Keller, 1985; Ullmann and Wendorff, 1979).

From Figure 6, it can be observed that the diffractogram of pure PP has five sharp diffraction lines corresponding to 110α, 040α, 130α, with some overlapping of the 111α, 131α and 041α planes, which are located at 2θ scattering angles of 14.1°, 17.0°, 18.8°, and 21.2°, respectively. The pattern indicates that only the α-form of crystalline structure is present because there is no line at 2θ of 16.0° which is generally associated with the β-form (Sun *et al.*, 2008; George *et al.*, 2000). Irrespective of the influence of the ratio of sulfur to peroxide, blending 60 parts of NR into 40 parts of pure PP to prepare the polymer blend, a decrease in the intensity of the five sharp crystalline peaks from the pure PP pattern can be clearly seen. Furthermore, a new crystalline peak with quite a weak intensity appears at a 2θ scattering angle of 16.0° corresponding to the β-pseudohexagonal structure. This decrease in intensity is attributable to the addition of the rubber material to the semi-crystalline thermoplastic, the rubber particles generally passing through and being present in the inter- and intra-spherulitic region of the crystalline component of the thermoplastic phase (Ghosh *et al.*, 1996; Martuscelli *et al.*, 1982). NR particles may possibly be trapped inside the spherulites of the PP suppressing the perfect growth of α-crystalline forms and correspondingly reducing the crystallinity. The reduction of the percentage crystallinity, X_c was confirmed by calculation of the area under the crystalline and amorphous portions as described above in the Section: X-ray diffraction studies. Table 3 shows the total degree of crystallinity of the PP in the NR/PP TPVs to be lower than that in pure PP. However, the presence of rubber particles cannot explain the occurrence of the β-forms. Generally, β-crystalline structures can be caused by various factors during crystallization, such as a temperature gradient, oriented melting prior to crystallization, adding a selective β-nucleating agent, or magnetic or electrical induction (Hou *et al.*, 2006). Although the use of fully-vulcanized powdered rubber particles as a β-nucleating agent has been reported (Sun *et al.*, 2008; Varga, 2002), these must be of ultrafine grade, smaller than 0.1 μm, which does not correspond to the size of the NR particles in the NR/PP TPVs in this study, seen in the SEM images.

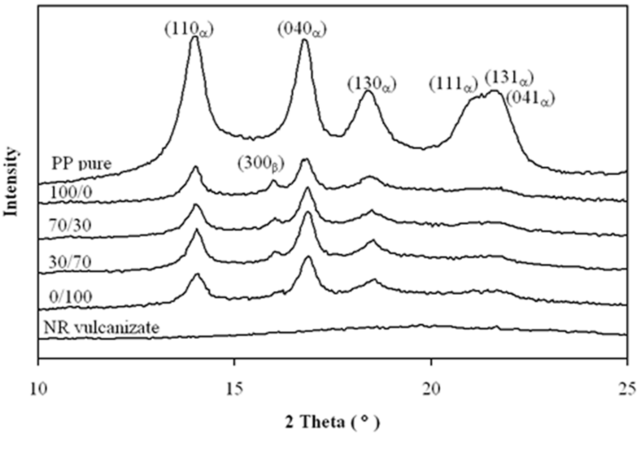

Figure 6. XRD patterns of NR/PP TPVs with various ratios of sulfur to peroxide in the mixed sulfur/peroxide vulcanization system in comparison with pure polypropylene and natural rubber vulcanizate.

Flow-induced crystallization in the injection molding and the simultaneous temperature gradient might be causing the β-crystalline structures (Kim *et al.*, 2005; Fujiyama *et al.*, 2000). The crystallization behavior of injection-molded PP in a temperature profile program (i.e., several times being heated up to a maximum melting temperature, and being cooled to a lower temperature) results in an alteration in the PP crystallization. This is apparently due to stress experienced during injection, flow behavior in the mold, and changes in the orientation of the molten PP on the surface of the injection-molded product, which result in a small crystalline size. However, these phenomena still need further investigation.

With regard to the NR/PP TPVs produced using mixed sulfur/peroxide vulcanization systems, the effect of the proportions of sulfur and peroxide on the crystallinity level and pattern can be observed in Table 3, which shows an increased percentage of crystallinity corresponding to an increased proportion of peroxide up to 70 parts. The explanation for this is the same as that adduced in the discussion of rheological properties that is that the peroxide curing agent in the mixed system increases the generation of free radicals in the PP phase and causes chain scission of the PP molecular chains resulting in a lowering of the molecular weight of the PP. The higher the peroxide content, the higher the PP degradation obtained. Decreased chain length provides a higher tendency to orient the crystallization process, because fewer restrictions are imposed by chain entanglements (Babu *et al.*, 2006a; Babu *et al.*, 2006b). A similar result was reported by George *et al.* (2000).

Table 3. Degree of crystallinity and $K_{\hat{a}}$ value of PP in the 60/40 NR/PP TPVs

Proportions of sulfur/peroxide	Crystallinity, X_c (%)	$K_{\hat{a}}$ value
PP (polypropylene) pure	53.0	0.00
100/0	40.0	0.17
70/30	42.5	0.14
30/70	49.3	0.11
0/100	43.5	0.06

Interestingly, when using a peroxide vulcanization system (0/100) the crystallinity of the PP decreases. This is attributable to competitive reactions caused by co-agents. In addition to the curing mechanism, the addition of co-agents contributes to the enhancement of side reactions in the thermoset co-agents domains and the co-agents homopolymer network (Figure 4). These combined effects result in the suppression of the spherulitical growth of the PP and hence, decrease the crystallinity.

Furthermore, undesirable polymers from co-agents cause deterioration in the properties of the TPVs. For β–form crystalline structures, the relative β–form value K_β was calculated and the data are shown in Table 3. The K_β value is zero in the absence of the beta form and is one if only the beta-form is present in the PP. It can be seen that the K_β value continues to decrease with the peroxide concentration, indicating a decrease in the amount of β-crystalline structures. As previously discussed, increasing the proportion of peroxide causes a reduction in the cross-link density and lowers the molecular weight of the PP. Differences in the viscosity of the melt components and rubber particles in the TPVs produced using different proportions of peroxide yield different apparent stress on the oriented melt dur ing injection and flow in the mold. This explains the observation of β-form structures in the data.

The change in the peak position and the interplanar spacing (d-value) of the crystalline patterns was also investigated. The data summarized in Table 4 indicate that incorporating NR into PP causes a very small shift in the 2θ scattering angle of the α-crystalline pattern to a higher level and reduces the d-values when compared with pure PP. However, it could be observed that among all the TPVs, there was no large change noted in d-values. This is because in this study, the blend ratio of the TPVs was fixed at 60/40 parts of NR/PP. However, a slight reduction in d-value was noted for the α-monoclinic structure at the reflections of the (040) and (130) planes and for the β-pseudohexagonal structure at a reflection of the (300) plane. This means that the distance between planes was reduced with the proportion of peroxide. The crystallinity pattern can be inferred from the change in the position of the peaks, whereas the intensity of the peaks indicates the level of crystallinity. Therefore, from the XRD evidence, it can be concluded that the incorporation of NR does not affect the general crystalline structure of PP; i.e., the composition retains the same α-monoclinic pattern of pure PP. But the crystallites are likely to be composed of somewhat defective, thinner lamellar crystals (Babu *et al.*, 2008) and the flow-induced crystallization and temperature gradient possibly promote extra β-form crystalline structures in the PP.

3.4 Differential scanning calorimetry measurements

DSC measurement was also conducted to study the crystallinity of the NR/PP TPVs. The DSC data are summarized in Table 5. Differential scanning calorimetry provides information about the micro-structural changes which take place in phases with varying proportions of peroxide in the curing system. It was found that with the incorporation of NR into the PP phase, the presence of NR particles in the spherulitic region of the PP caused defects in the formation of PP crystallinity. As a result, a reduction of the melting enthalpy of the crystallinity (ΔH_{TPVs}) and the percentage crystallinity (X_i) was observed, in comparison to pure PP. Further, the DSC data fluctuated somewhat with changes in the proportion of peroxide in the mixed curing system. ΔH_{TPVs} and X_i were observed to increase with the proportion of peroxide until it reached a maximum value at 70 parts of peroxide; thereafter they decreased. This means that peroxide plays a

Table 4. Data of the scattering angle (2θ) and the interplanar distance (d value) of PP crystalline in the 60/40 NR/PP TPVs

Proportions of sulfur/peroxide	Reflection									
	110		040		130		111, 131, 041 overlapping		300	
	2θ (°)	d (Å)	2θ (°)	d (Å)	2θ (°)	d (Å)	2θ (°)	d (Å)	2θ (°)	d (Å)
PP (polypropylene) pure	13.96	6.34	16.81	5.28	18.33	4.84	21.75	4.09	-	-
100/0	14.03	6.31	16.82	5.27	18.42	4.82	21.65	4.10	15.99	5.54
70/30	14.04	6.31	16.84	5.27	18.47	4.80	21.65	4.10	16.02	5.53
30/70	14.06	6.30	16.88	5.25	18.48	4.80	21.71	4.09	16.06	5.52
0/100	14.05	6.31	16.85	5.26	18.53	4.79	21.62	4.11	16.20	5.47

Table 5. DSC data of 60/40 NR/PP TPVs with varying proportions of sulfur and peroxide

Proportions of sulfur/peroxide	ΔH_{TPVs} (J/g)	X_i (%)
PP (polypropylene) pure	70.70	33.8
100/0	19.37	23.2
70/30	19.50	23.3
30/70	24.00	28.7
0/100	20.74	24.8

role in changing the microstructure of the PP. Higher peroxide content causes more PP degradation; this decrease in chain length means less restriction by chain entanglements, leading to an increased crystallinity of the PP in the NR/PP TPVs. The peroxide vulcanization system creates the reverse trend in crystallinity of other TPVs. This results from side reactions due to the presence of co-agents which possibly form a thermoset network domain and homopolymers which reduce the ability of spherulites to grow and hence, decrease the crystallinity. The DSC data observed in this section are in agreement with the percentage crystallinity measured by X-ray diffraction.

4. Conclusion

The influence of mixed sulfur/peroxide vulcanization systems on the properties of dynamically vulcanized NR/PP blends was studied experimentally while varying the proportions of sulfur and peroxide. The peroxide fraction caused cross-linking of the NR chains and simultaneously promoted severe chain scission in the PP molecules. Thus changes in this fraction caused variation in the macroscopic rheological properties, morphology and crystallinity of the NR/PP TPVs produced. Further, micro-structural changes in the structure of the dispersed NR particles, the percentage crystallinity, and the crystalline structure were observed as well as changes in the phase morphology of the NR/PP TPVs, which explain the macroscopic observations. Among the mixed systems, dynamic vulcanization using a sulfur to peroxide ratio of 70/30 produced near optimal overall properties of the TPV.

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