

Influence of Phenolic Curative on Crosslink Density and Other Related Properties of Dynamically Cured NR/HDPE Blends

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ABSTRACT: Dynamically cured 60/40 NR/HDPE blends with various amounts of phenolic curative were prepared in an internal mixer at 160°C. A simple blend (i.e., the blend without curative) was also prepared using the same materials and blend proportion for comparison purposes. Mechanical, dynamic, and morphological properties; swelling resistance and crosslink density of the blends were investigated. It was found that the thermoplastic vulcanizates (TPVs) gave superior mechanical and dynamic properties than the simple blend. Furthermore, the mechanical properties in terms of elongation at break, modulus and tensile strength and elastic response in dynamic test in terms of storage modulus increased with increased loading amount of the curative. The complex viscosity also increased but the $\tan \delta$ and tension set decreased with increased loading level of the curative. The crosslink density of the TPVs was estimated based on the elastic shear modulus. It was found that the crosslink den-

sity of the blends increased with increased loading levels of the curative while the degree of swelling decreased. This correlated well with the trend of mechanical and dynamic properties. SEM micrographs were used to confirm the level of mechanical and dynamic properties. It was found that the simple blend at a given blend ratio exhibited co-continuous phase morphology. However, the TPVs showed micron scale of vulcanized rubber domains dispersed in a continuous HDPE matrix. The size of vulcanized rubber domains decreased with increasing amounts of the curative. This led to greater interfacial adhesion between the phase and hence superior mechanical and dynamic properties. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1232–1240, 2009

Key words: natural rubber (NR); polyethylene; phenolic curative; mechanical; morphological properties; crosslink density

INTRODUCTION

Thermoplastic vulcanizates (TPVs) are blends of rubber and thermoplastic components where the elastomer component is vulcanized *in situ* during melt mixing at high shear and elevated temperature. Dynamic vulcanization allows the crosslinked elastomer to become the dispersed phase even in cases where the elastomer is a major component. That is, where the volume fraction of elastomeric phase is greater than 0.5. During dynamic vulcanization, abrupt increasing of shear and extensional viscosities of the vulcanizing elastomer phase occurs. As a consequence, the phase evolution takes place as the elastomer break-up into smaller particles and

becomes the dispersed phase in the thermoplastic matrix. Ultimate elongation and tensile strength of TPVs depend upon the crosslinking concentration of the rubber phase and the dispersion morphology in terms of the rubber domain sizes and distributions.^{1,2} Degree of crosslinking in the rubber phase could have profound effects on viscosity during mixing with the thermoplasticity and elasticity of the final products. Various parameters which influence morphological properties of the TPVs include vulcanization system³ curative contents,^{4,5} and mixing conditions.⁶ The crosslink density is also an extremely important factor in determining physical properties of the dynamic vulcanizates. This is evident for almost all mechanical properties, e.g. modulus, hardness, tear and tensile strength, creep, relaxation and compression set. For this reason, crosslink density is of major interest for the production and use of this material. Until now, there have been only a few methods available for determination of crosslink density of in TPVs.^{1,7–9} Few works have looked at the effect of various curing agents, such as phenolic resin, peroxide, and mixed sulfur-peroxide,

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on the morphology, rheology, and dynamic mechanical properties of polyolefinic blend systems.^{1,10–12} However, the crosslink density often describes relatively to those properties without determination of the absolute values.

Crosslink density of natural rubber and styrene butadiene rubber (SBR) have been estimated by using a newly developed rheometer, the Rubber Process Analyzer (RPA 2000) which was designed specially to measure dynamic properties such as shear modulus (G') and shear loss modulus (G'') in cured and uncured rubber.^{13,14}

Therefore, the crosslink density of TPVs is possible to estimate using elastic shear modulus based on the dynamic test. Vulcanization of rubber and dynamically cured rubber phase caused two types of crosslink density: physical (χ_{phy}) and chemical crosslink density (χ_{chem}). It is important to distinguish between physical (χ_{phy}) and chemical crosslink density (χ_{chem}) which results directly from vulcanization. Langley¹⁵ has shown that these are expressed as $\chi_{\text{phy}} = \chi_{\text{chem}} + \chi_{\text{int}}$ where χ_{int} is the initial crosslink density due to entanglements, constraints or other effects not due to chemical changes. Assuming χ_{int} after vulcanization is same as χ_{int} before vulcanization, χ_{chem} is the difference between crosslink density measured on a specimen before vulcanization. Therefore, χ_{chem} is the difference between crosslink density measured on the specimen before and after vulcanization.¹⁴ Determination of crosslink density of the TPVs from the dynamic test using the Flory equation as given below

$$G' = 2RTX_{\text{phy}} \quad (1)$$

where, G' is elastic shear modulus, R is the gas constant, T is the absolute temperature and X_{phy} is the crosslink density, respectively.

While χ_{int} can be envisaged as the crosslink density of the uncured rubber. This related to the plateau shear modulus (G_N^0) of the rubber network.¹⁶

$$G_N^0 = g_N 2X_{\text{int}}RT \quad (2)$$

where g_N is a front factor, R is the gas constant and T is the absolute temperature.

G_N^0 corresponds to the $G'(\omega)$ value of the frequency-independent segment (plateau zone) of the curves in uncured rubber.

After crosslinking, the theory of rubber elasticity states

$$G_e = g_e 2X_{\text{phy}}RT \quad (3)$$

where G_e is the equilibrium modulus of the crosslinked network, R is the gas constant and T is the absolute temperature. Within the scope of this work we assume, g_N equals to g_e . In dynamic testing, G' and G'' can be measured on a specimen while the

network is being formed. To simplify the calculation of χ_{chem} and χ_{phy} from G' values before and after curing, the following assumptions are considered.

- (1) G_N^0 can be approximated as G' measured at 5 Hz, while testing an uncured specimen.
- (2) G_e can be approximated as G' measured at 0.5 Hz, while testing a fully cured specimen.

Finally, from eqs. (2) and (3), X_{chem} becomes

$$X_{\text{chem}} = \frac{G'_{\text{cured}}(0.5 \text{ Hz}) - G'_{\text{uncured}}(5 \text{ Hz})}{2RT} \quad (4)$$

In this present study, eq. (4) was used to determine the crosslink density of dynamically cured 60/40 NR/HDPE TPVs. The corresponding increase in effective crosslink density with curative content in the TPVs was confirmed by mechanical, dynamic, solvent swelling, and morphological properties. Meanwhile, the evolution of blend morphology was investigated in the blends with various loading levels of phenolic curative.

EXPERIMENTAL

Materials

The natural rubber, air-dried sheet (ADS) used as the rubber component was manufactured by Khun Pan Tae Farmer Cooperation (Phattalung, Thailand). High density polyethylene (HDPE), used as a blend composition, was manufactured by the Thai Polyethylene, Co., Ltd, (Rayong, Thailand). It was an injection molding grade, H6007J with melt flow index (MFI) of 7.5 g/ 10 min (2.16 kg loads at 190°C) and density of 970 kg m⁻³. Phenolic modified HDPE compatibilizer (here referred to as PhHRJ-PE) was prepared in-house using HDPE, phenolic resin with active hydroxymethyl (methylol) groups (HRJ-10518, manufactured by Schenectady International Inc., New Port, USA) and stannous chloride or tin (II) chloride hydrate (SnCl₂·2H₂O) catalyst. The preparation and characterization procedure of PhHRJ-PE were described elsewhere^{17,18} The same type of phenolic resin and catalyst was also used as a curative of the rubber component in the dynamic vulcanization process. The zinc oxide and stearic acid were manufactured by Global Chemical Co., Ltd, Samutprakarn, and Imperial Chemical Co., Ltd, Pathumthani Thailand. The polyphenolic additive, Wingstay[®] L, used as an antioxidant was manufactured by Eliokem Inc., Ohio, USA.

Compounding of NR

Oil extended natural rubber (i.e., OENR) was first prepared by mixing the NR with 30 phr of white oil

TABLE I
Compounding Formulation and Mixing Schedule

Ingredients	Quantity (phr)	Mixing schedule (min)
OENR (with 30 phr of oil)	130	5
Stearic acid	1.0	1
ZnO	5.0	2
Wingstay L	1.0	1
SnCl ₂ ·2H ₂ O	Various doses ^a	1
Phenolic resin (HRJ-10518)	Various doses ^b	2

^a 0, 3, 5 and 7 phr.

^b 0, 0.36, 0.6 and 0.84 phr.

(Conocophillips Co., Ltd., USA) in a 3-L dispersion kneader at 80°C (Yong Fong Machinery Co., Ltd, Samutsakorn, Thailand). The OENR was then compounded using a phenolic vulcanization system. The compounding was performed on a two-roll mill at room temperature using a compounding formulation and mixing schedule as shown in Table I. Various doses of phenolic curative and catalyst were each used in this work. The rubber compound were later sheeted out and conditioned at room temperature in a closed container for 24 h before dynamic vulcanization while blending with HDPE.

Preparation of 60/40 NR/HDPE TPVs

The dynamically cured NR/HDPE TPVs were prepared using an internal mixer with a mixing chamber of 500 mL at 160°C and a rotor speed of 60 rpm. The blend proportion was fixed at NR/HDPE = 60/40. The process started by warming HDPE in the mixing chamber for 6 min without rotation and followed by mixing the HDPE at a rotor speed of 60 rpm at 160°C for 4 min. The blend compatibilizer (i.e., PhHRJ-PE) at a loading level of 5 wt % of HDPE was incorporated and mixed for another 1 min. Finally, the OENR compound was added into the mixing chamber and the mixing was continued until fully vulcanized. The blending product was then cooled down to room temperature and cut into small pieces using a Bosco plastic grinder (Bosco Engineering Co., Ltd., Samutparkarn, Thailand).

Mechanical properties

Dumbbell samples were prepared by thermoplastic injection molding using a machine with a clamping force of 90 tons (Welltec Machinery Ltd., Hong Kong). Tensile properties of the TPVs were measured at 23°C using 2-mm thick injection molded samples per ISO-standard according to ASTM D412. Hounsfield tensometer (model H 10KS) was used at 500 mm/min. Tensile properties in terms of tensile strength, modulus, and elongation at break were determined. Tension set values at 100% elongation

were determined at room temperature according to ISO 2285. The samples were kept under tension for a fixed elongation and time interval (i.e., 100% and 10 min, respectively). The test specimens were then released and conditioned for another 10 min. The dimensions were eventually determined compared with the original shapes. Shore A durometer hardness of the samples was also measured according to ISO 7619.

Dynamic properties

Dynamic properties of 60/40 NR/HDPE TPVs were characterized using a rotorless oscillating shear rheometer (RheoTech MDPT, Cuyahoya Falls, USA) at 160°C. The oscillation frequency was set in the range of 0.1–200 rad/s at a constant strain of 3%. This was to assure the range of linear viscoelasticity during the test. The storage (G') and loss shear (G'') modulus, loss factor, $\tan \delta = G''/G'$ as well as the complex viscosity (i.e., $\eta^* = 3G^*/\omega$, $\omega = \eta'' + i\eta'$) of the TPVs were characterized.

Crosslink density

A rotorless oscillating shear rheometer (RheoTech MDPT) was used to measure the storage shear modulus (G') of the simple blend and TPVs based on 60/40 NR/HDPE blends at 160°C, at 3% strain and a frequency of 0.5 Hz. The storage shear modulus of the uncured simple blend and dynamically cured TPVs was then used to determine the crosslink density as described in eq. (4).

Swelling measurement

Swelling of 60/40 NR/HDPE TPVs was examined in IRM903 oil according to ASTM D471. Rectangular specimens with dimensions of $10 \times 10 \times 3 \text{ mm}^3$ were first immersed in IRM903 at room temperature for 166 h. Swollen samples were separated and blotted with tissue paper and immediately transferred into a weighing container to determine swollen weight. The weight gains, or swelling, were then determined as follow:

$$\text{Swelling (\%)} = \left[\frac{(W_2 - W_1)}{W_1} \right] \times 100 \quad (5)$$

where W_1 is initial mass of specimen (g) and W_2 is the mass of specimen after oil immersion (g).

Morphological characterization

Morphological studies were carried out using a Leo scanning electron microscope, model VP 1450, manufactured by Leo Co., Ltd., Cambridge, UK. Injection molded samples of the TPVs were first cryogenically

cracked in liquid nitrogen to avoid any possibility of phase deformation during the cracking process. The fractured surfaces were then etched by means of extraction with hot xylene at approximately 80°C for 30 min to remove the HDPE phase. The samples were later dried in vacuum oven at 40°C for 3 h to eliminate the contamination of the solvent. The dried surfaces were later gold-coated and examined by scanning electron microscopy.

RESULTS AND DISCUSSION

Mechanical and morphological properties

Stress–strain curves of dynamically cured 60/40 NR/HDPE containing different levels of phenolic curative are shown in Figure 1. It can be seen that the uncured blend (i.e., the blend without curative) shows higher initial slope of the curve (i.e., Young's modulus). This reflects higher stiffness of the material. However, this type of blend exhibited lower stress or strength at failure position. It is also seen that the yielding phenomena were absent in the TPVs with curative in particular loading levels of the phenolic curative (i.e., at 5 and 7 phr). Furthermore, superior tensile strength and elongation at break were observed in the TPVs with higher levels of the curative. This is attributed to the influence of dynamic vulcanization via the phenolic curative molecules which thereafter caused stronger materials. The total area under stress–strain curves, which represents the toughness of material, also increased with increasing loading levels of the phenolic curative. This result revealed that the TPVs exhibited higher rubber elasticity than that of the blend without curative. This can be ascribed in terms of domain sizes and dispersion of vulcanized rubber domains dispersed in the continuous HDPE matrix. At the mixing conditions, the crosslinking reaction

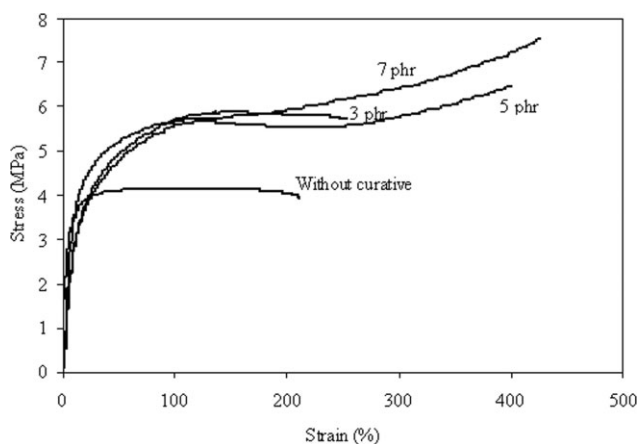


Figure 1 Stress–strain curves of 60/40 NR/HDPE blends without curative and dynamically cured TPVs using various loading levels of phenolic curative.

occurs through the free methylol and hydroxyl groups of phenolic resin with the unsaturation in the NR molecules in the presence of stannous chloride, as reaction mechanism described in our previous work.¹⁸ Also, it was proved that an increase in interfacial adhesion in vulcanized rubber domains and matrix is caused by incorporation of PhHRJ-PE compatibilizer into the blends. This caused a formation of compatibilizing block copolymers of NR and HDPE at the interface of NR and HDPE.¹⁸ This promoted the greater elastomeric nature in the TPVs compared with the blend without curative (i.e., a simple blend). These results were confirmed by SEM micrograph, as shown in Figure 2. The simple blend (i.e., without crosslinking agent) shows the co-continuous phases of NR and HDPE [Fig. 2(A)]. This type of TPE exhibited rubber elasticity but was not as good as the TPVs of the same blend proportion. Upon addition of the phenolic curative, the tensile deformation pattern in Figure 1 changes drastically. That is, the weak elastomeric material of the simple blend gradually changes to a stronger and tougher material (i.e., TPVs) as a result of dynamic vulcanization. The addition of the curative resulted in a crosslinking reaction of the rubber molecules and thereby the viscosity increased. On subsequent shearing, more effective rubber particle break-up took place and led to a significant change in morphology, as evidenced in Figure 2(B–D). The rubber particle break-up during dynamical vulcanization has been described as low shear deformation to act as the main mixing mechanism, but elongational deformations are required as a precondition for effective dispersion. Therefore, the elongational flow appeared to produce more effective break-up and dispersion than rotational shear flow.¹⁹ As a result, a co-continuous phase morphology at the beginning of the mixing process was a prerequisite to generate the dispersed phase morphology of the vulcanized rubber at the end. During mixing, the viscosity of rubber phase became very high immediately after introducing curing agents. As a result, the stresses in the material increased very strongly, leading to the break-up of the co-continuous rubber into small particles.²⁰ The crosslinking of rubber molecules increased the viscosity of the rubber particles and prevented the coalescence of the particles. Increasing loading level of phenolic curative in the rubber compound caused increasing torque of the curing curves, as shown in Figure 3. This is evidence of increasing viscosity of the same compound during dynamic vulcanization with HDPE. In Figure 2, it is seen that the TPVs are a two-phase system with dispersed vulcanized rubber domain in the continuous HDPE matrix. Size of rubber domains decreased with increasing amounts of curative from approximately 2 μ in the TPV with 3 phr of phenolic

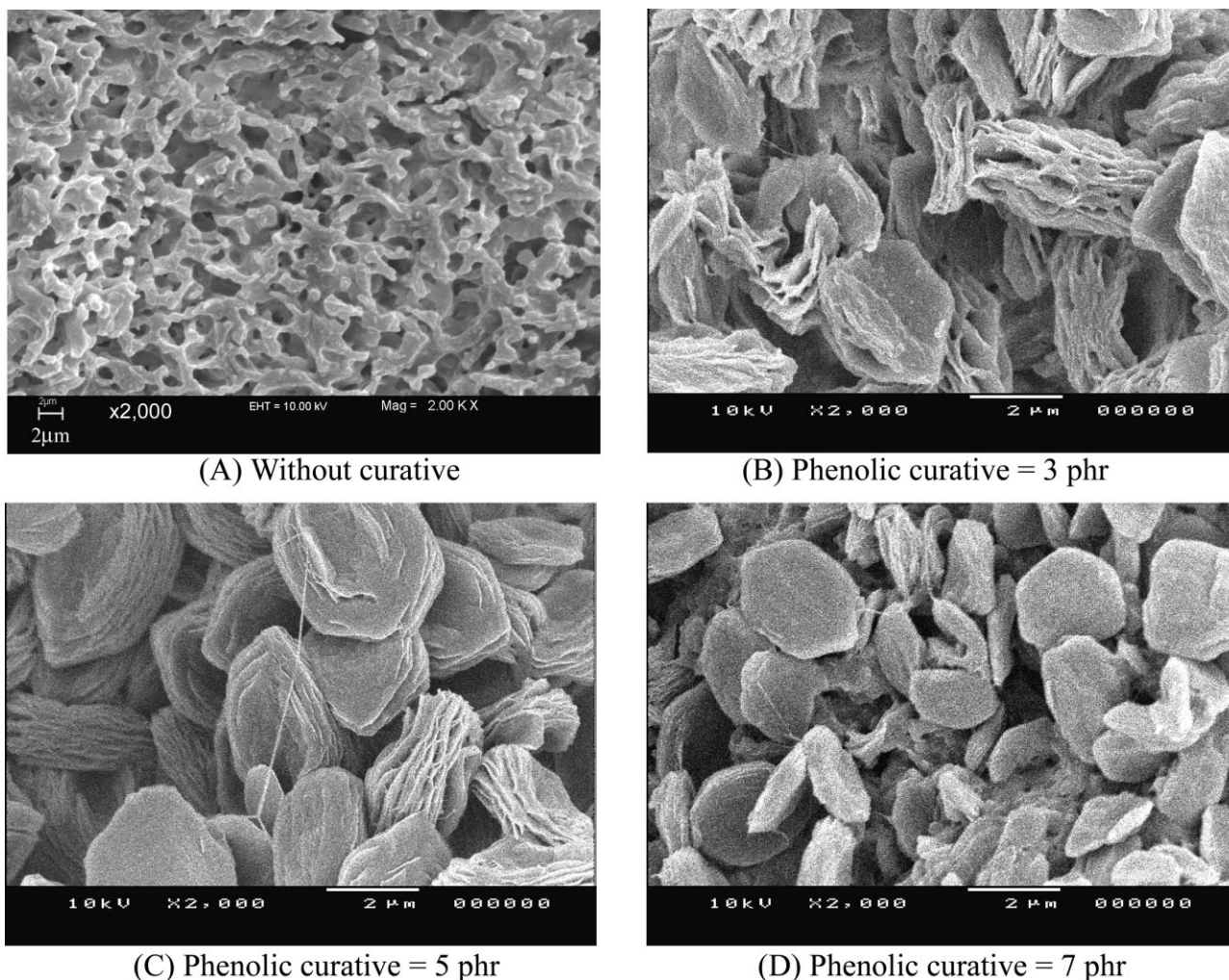


Figure 2 SEM micrographs of 60/40 NR/HDPE blends without curative and dynamically cured using various loading levels of phenolic curative; (A) without curative, (B) 3 phr, (C) 5 phr, and (D) 7 phr of phenolic curative.

curative to approximately $1\ \mu$ for the TPV with 7 phr of curing agent. A large number of small and more uniformly distributed crosslinked rubber particles were observed in the TPV with increasing loading levels of the curative. This causes increasing interfacial areas and hence interfacial adhesion between different phases by compatibilizing effect of PhHRJ-PE compatibilizer. Also, the entangled rubber molecules in the rubber domains could not slip past each other resulting in higher mechanical strength and elastomeric properties of the TPVs.

Figure 4 shows tensile strength and elongation at break of the TPVs with various loading level of phenolic curative. It can be seen that the TPVs exhibited higher tensile strength and elongation at break than that of the simple blend (i.e., at concentration of phenolic curative = 0 phr). The increase is more pronounced for the TPVs with higher loading levels of the phenolic curative. This is attributed to the increased crosslink density with increased loading levels of the phenolic curative. The increase in

tensile strength is also due to the increased chain entanglements caused by an increasing degree of crosslinking and hence crosslink density, as shown

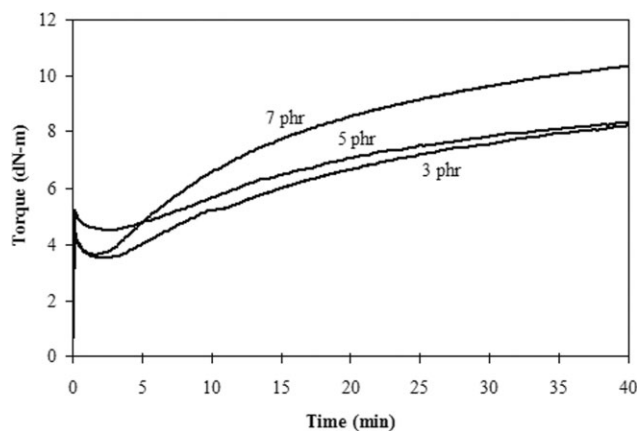


Figure 3 Curing curves of NR compounds using various loading levels of phenolic curative.

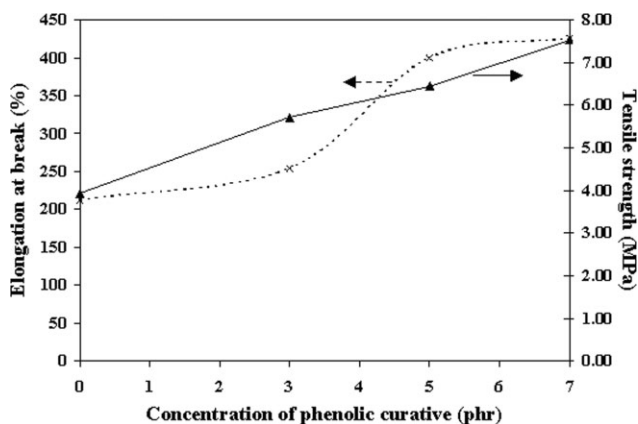


Figure 4 Tensile strength and elongation at break of 60/40 NR/HDPE blends without curative and dynamically cured TPVs using various loading levels of phenolic curative.

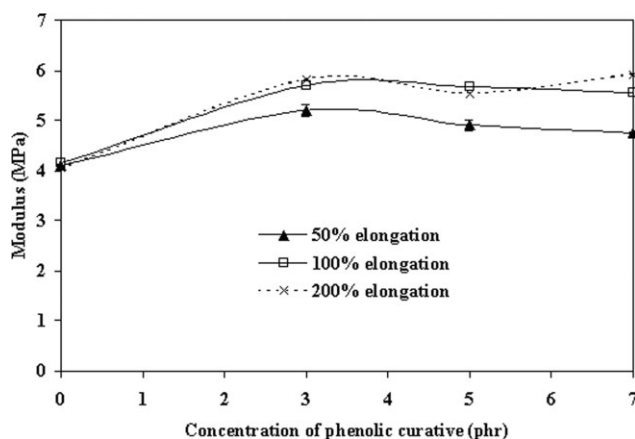


Figure 6 Tensile modulus at 50, 100, and 200% elongation of 60/40 NR/HDPE blends without curative and dynamically cured TPVs using various loading levels of phenolic curative.

in Figure 5. That is, the crosslink density increased with increasing loading level of the phenolic curative in the blends while the degree of swelling in the IRM903 oil decreased. It is therefore concluded that the higher degree of crosslinking in the TPVs caused increasing tensile strength but decreased degree of swelling in the IRM903 oil. This result agrees with previous work²¹⁻²⁴ which stated that the TPVs exhibited higher tensile strength than corresponding unvulcanized blends. In Figure 4, the elongation at break also increased with increasing crosslink density (Fig. 5) as the crosslinked rubber particles can be strained to very long dimension to failure. The crosslink also attributed to the flexibility of the rubber molecules under applied stress.

Figure 6 shows the tensile modulus of the NR/HDPE blend at 50, 100, and 200% elongation. It is seen that the modulus at a given elongation of the TPVs are higher than that of the simple blend counterpart. The modulus of TPVs was marginally

changed with increasing content of the curative to 3 phr. However, further increasing loading level of the phenolic curative to higher than 3 phr caused insignificant change in the modulus value of the TPVs. Therefore, it is concluded that loading level of the curative did not play a significant role on magnitude of the tensile modulus.

Figure 7 shows tension set of dynamically cured 60/40 NR/HDPE compared with the simple blend at the same blend proportion. Tension set value has been used to characterize the elastomeric properties of the TPE products. In the case of a conventional rubber vulcanizate, the tension set or other type of set properties such as compression set value is mainly related to the crosslink density of the vulcanized rubber. However, in the TPE materials which are composed of two-phase morphology, the tension set is not only related to the crosslink density of the elastomer phase, but also depends on properties of the thermoplastic matrix. In Figure 7, it is seen that

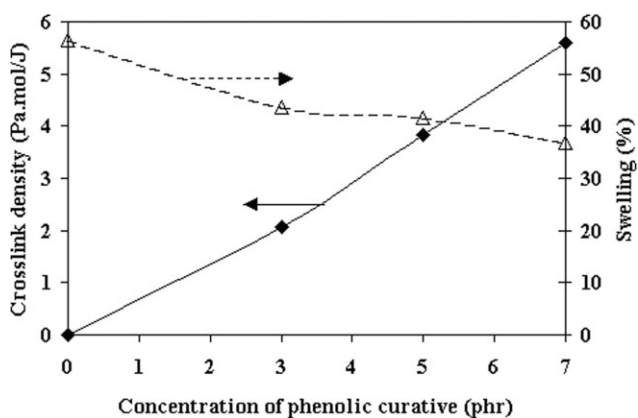


Figure 5 Crosslink density 60/40 NR/HDPE blends without curative and dynamically cured 60/40 TPVs using various loading levels of phenolic curative.

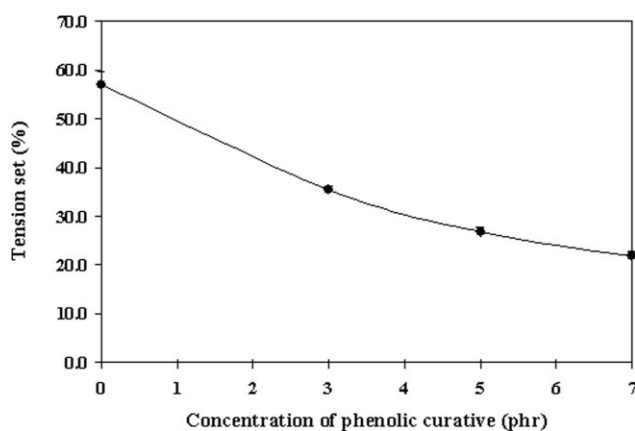


Figure 7 Tension set of 60/40 NR/HDPE blends without curative and dynamically cured TPVs using various loading levels of phenolic curative.

the uncured material (i.e., the simple blend) exhibited the highest tension set value indicating inferior elastomeric properties or elastic response. Furthermore, the set values clearly decreased with increasing loading levels of the phenolic curative. This is attributed to the morphology changes because of the dynamic vulcanization (Fig. 2). That is, the uncrosslinked TPE sample based on a simple blend exhibited a co-continuous phase morphology of NR and HDPE phases which gave the higher tension set value of 57%. That is, material shows lower tendency to recover to the original shape after prolonged extension. Significant improvement of tension set properties were observed in the dynamically cured TPVs with increasing amount of the curative as the smaller rubber particles dispersed in continuous HDPE matrix. The TPV containing the highest curative content exhibited the lowest tension set value of 22%. This confirms better elasticity of the TPV materials.

Dynamic properties

Figure 8 shows the storage shear modulus (G') as a function of frequency. It is seen that the blends show an increase in G' with increasing frequency. This is due to the decrease in time available for molecular relaxation. Also, at a given frequency, the G' values increased with increasing loading levels of curative, as shown in Figure 9. In this system, the dynamic test was performed at 160°C where the HDPE matrix was completely melted, while the vulcanized rubber domains remained un-melted particles. Therefore, the elastic properties of the system greatly depend on the properties of vulcanized rubber domains. As a consequence, higher elastic response (i.e., storage modulus) was observed for the samples with higher amounts of curative and

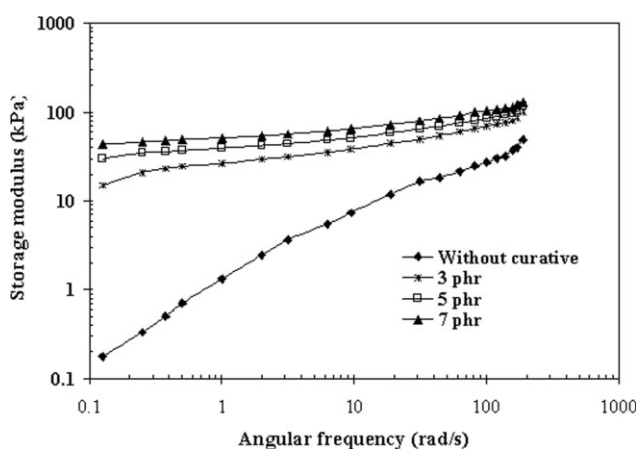


Figure 8 Storage modulus as a function of frequency of 60/40 NR/HDPE blends without curative and dynamically cured TPVs at 160°C.

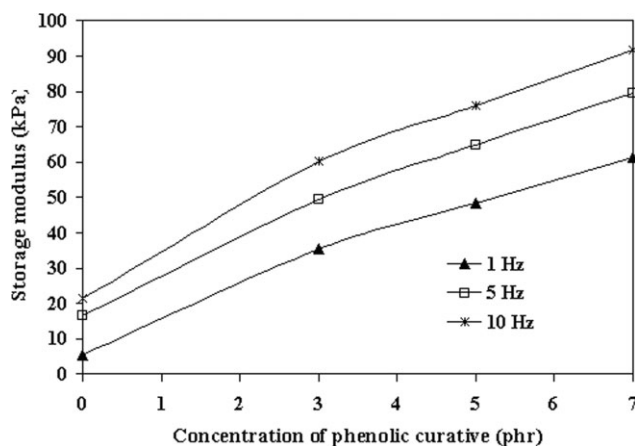


Figure 9 Storage shear modulus of 60/40 NR/HDPE blends without curative and dynamically cured 60/40 TPVs using various loading levels of phenolic curative.

thus small particles of vulcanized rubber. According to the SEM micrographs in Figure 2, the higher loading levels of phenolic curative caused the smaller vulcanized rubber domains and HDPE cavitations. Smaller rubber domains provide higher surface areas and hence interfacial force to promote interaction between NR and HDPE phase with the compatibilization of the blend compatibilizer (i.e., PhHRJ-PE). This results in increasing of elastic modulus with increasing curative content.

Figure 10 shows the $\tan \delta$ as a function of frequency of 60/40 NR/HDPE blends. The $\tan \delta$ is a ratio between loss modulus and storage modulus or the ratio of viscous and elastic properties (i.e., $\tan \delta = G''/G'$). It is seen that the TPVs exhibited lower $\tan \delta$ values than that of the simple blend. That is, the TPVs showed greater elastic response than that of the simple blend which corresponds to the storage shear modulus in Figure 8. This is attributed to the immobilization of the NR particles by crosslinking and thereafter breaking down into smaller size under the applied shear field.¹⁰ Therefore, the TPVs

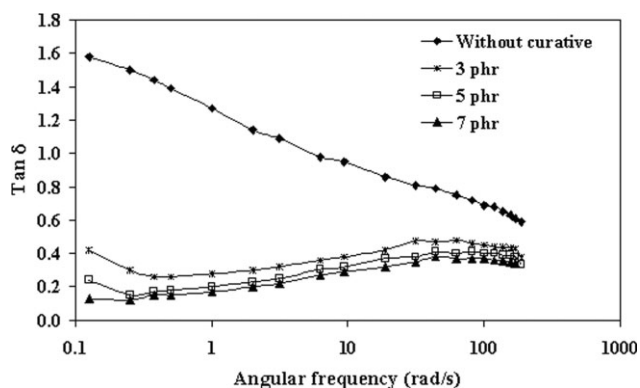


Figure 10 $\tan \delta$ as a function of frequency of 60/40 NR/HDPE blends without curative and dynamically cured TPVs at 160°C.

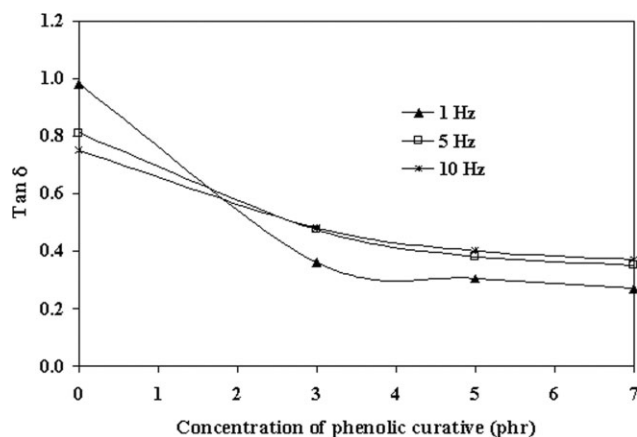


Figure 11 $\tan \delta$ of 60/40 NR/HDPE blends without curative and dynamically cured TPVs using various loading levels of phenolic curative.

showed greater elastic character which gave better mechanical properties than that of the simple blend. Also, the TPVs with higher curative content exhibited lower $\tan \delta$ values or damping factor corresponding to the lowest tension set in Figure 7. Therefore, the higher loading levels of curative, the greater elastic response becomes. This trend of $\tan \delta$ in Figure 11 agrees with the decreasing trend of tension set values in Figure 6. That is, the elastomeric properties of the TPVs increased with increasing content of curative.

Figure 12 shows the complex viscosity of the 60/40 NR/HDPE blends without and with various amounts of curing agent. It is clear that the viscosity of the blends is highly shear-sensitive with significant drops at higher angular frequencies or higher shear rate. This demonstrates that the melts are pseudoplastic and exhibit shear-thinning behavior. At high frequencies, the viscosity difference of the blends with different amounts of curing agent is smaller. This indicates higher molecular restrictions caused by formation of chemical crosslinks with

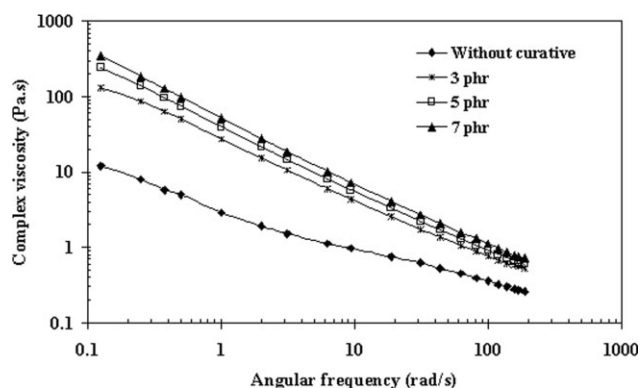


Figure 12 Complex viscosity as a function of frequency of 60/40 NR/HDPE blends without curative and dynamically cured TPVs at 160°C.

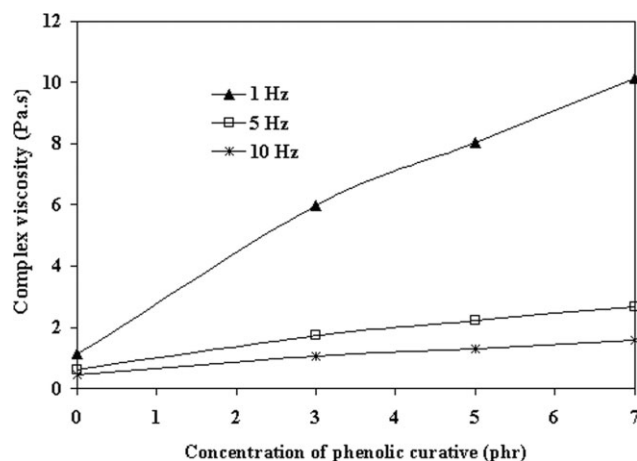


Figure 13 Complex viscosity of NR/HDPE blends without curative and dynamically cured 60/40 NR/HDPE TPVs using various loading levels of phenolic curative.

increasing phenolic resin. Furthermore, the melt viscosity at a constant frequency (Fig. 13) of the blends increased with increasing content of the curative. That is, higher flow resistance was observed. This can be attributed to the TPVs with smaller vulcanized rubber particles exhibiting higher interaction between the two phases because the higher surface area and thus higher interfacial adhesion.

CONCLUSION

The 60/40 NR/HDPE blends without curative and dynamically cured 60/40 NR/HDPE TPVs using various loading levels of phenolic curative were prepared. Influence of content of curative on mechanical, morphological, and dynamic properties, as well as crosslink density and degree of swelling were investigated. Increasing loading levels of curative caused increased elastic response in dynamic properties (i.e., storage modulus, complex viscosity, and $\tan \delta$), and mechanical properties in terms of tensile strength, elongation at break, and tension set. Also, the TPVs exhibited higher mechanical and dynamic properties than the simple blend. The TPVs consisted of two phases (i.e., vulcanized NR domains dispersed in HDPE phase) while the simple blend was also a two-phase system with co-continuous phase morphology. As the loading level of phenolic curing agent increased, the vulcanized NR phase changed to a smaller size of rubber domains in continuous HDPE phase. The crosslink density of the blend clearly increased with increasing contents of the curative while the degree of swelling decreased.

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References

1. Ellul, M. D.; Tsou, A. H.; Hu, W. *Polymer* 2004, 45, 3351.
2. Coran, A. Y.; Patel, R. P. In *Thermoplastic Elastomers*, 2nd ed.; Holden, G.; Legge, N. R.; Quirk, R.; Schroeder, H. E., Eds. Hanser: New York, 1996; Chapter 7, p 153.
3. Nakason, C.; Wannavilai, P.; Kaesaman, A. *J Appl Polym Sci* 2006, 100, 4279.
4. Vennemann, N.; Bokamp, K.; Broker, D. *Macromol Symp* 2006, 245, 641.
5. Naderi, G.; Nouri, M. R.; Mehmood, M.; Bakhshandeh, G. R. *Iran Polym J* 1999, 8, 37.
6. Thitithammawong, A.; Nakason, C.; Sahakaro, K.; Noordermeer, J. W. M. *Eur Polym J* 2007, 43, 4008.
7. Ellul, M. D.; Jaymini, P.; Tinker, A. J. *Rubber Chem Technol* 1995, 68, 573.
8. Setua, D. K.; Soman, C.; Bhowmick, A. K.; Mathur, G. N. *Polym Eng Sci* 2002, 42, 10.
9. Zhang, X.; Huang, H.; Zhang, Y. *J Appl Polym Sci* 2002, 85, 2862.
10. Xiao, H. W.; Huang, S. Q.; Jiang, T. *J Appl Polym Sci* 2004, 92, 357.
11. Neeraj, G. K.; Anil, J. K.; Singhal, R.; Nagpal, A. K. *J Appl Polym Sci* 2000, 78, 2104.
12. Nakason, C.; Wannavilai, P.; Kaesaman, A. *Polym Test* 2006, 25, 34.
13. Lee, S.; Pawlowski, H.; Coran, A. Y. *Rubber Chem Technol* 1994, 67, 854.
14. Chattaraj, P. P.; Mukhopadhyay, R. *Rubber Chem Technol* 1996, 70, 90.
15. Langley, N. R. *Macromolecules* 1968, 1, 348.
16. Pearson, D. S.; Graessley, W. W. *Macromolecules* 1980, 13, 1001.
17. Nakason, C.; Jarnthong, M.; Kaesaman, A.; Kiatkamjornwong, S. *J Appl Polym Sci* 2008, 109, 2694.
18. Nakason, C.; Nuansomsri, K.; Kaesaman, A.; Kiatkamjornwong, S. *Polym Test* 2006, 25, 782.
19. Grace, H. P. *Eng Commun* 1982, 14, 225.
20. Naskar, K. *Rubber Chem Technol* 2007, 80, 504.
21. George, S.; Joseph, R.; Thomas, S. *J Appl Polym Sci* 1995, 78, 2104.
22. Coran, A. Y.; Patel, R.; Willams, D.; Gummi, F. K. *Rubber Chem Technol* 1998, 39, 658.
23. Coran, A. Y.; Patel, R.; Willams, D. *Rubber Chem Technol* 1985, 58, 1014.
24. Elliot, D. J. In *Thermoplastic Elastomer from Rubber Plastic Blends*; De, S. K.; Bhowmick, A. K., Eds. Ellis Harwood: New York, 1990; Chapter 4.