Influence of Oil Contents in Dynamically Cured Natural Rubber and Polypropylene Blends

Charoen Nakason, Wisut Kaewsakul

Center of Excellence in Natural Rubber Technology, Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani 94000, Thailand

ABSTRACT: Mechanical, dynamic, thermal, and morphological properties of dynamically cured 60/40 NR/PP TPVs with various loading levels of paraffinic oil were investigated. It was found that stiffness, hardness, tensile strength, storage shear modulus, complex viscosity, glass transition temperature (T_g) of the vulcanized rubber phase, degree of crystallinity and crystalline melting temperature (T_m) of the polypropylene (PP) phase decreased with increasing loading levels of oil. This is attributed to distribution of oil into the PP and vulcanized rubber domains causing oil-swollen amorphous phase and vulcanized rubber domains. An increasing trend of elastic response in terms of tension set and damping factor was observed in the TPVs with loading levels of oil in a range of 0–20 phr. It is supposed that a major proportion of oil was first preferably migrated into the PP phase and caused an abrupt decreasing trend of degree of crystallinity and T_m of the PP phase. The dispersed vulcanized rubber domains remained small as particles with a low degree of swelling. Increasing loading levels of oil higher than 20 phr caused a decreasing trend of elongation at break and elastomeric properties. Saturation of oil in the PP phase was expected and the excess oil was transferred to the rubber phase which thereafter caused larger swollen vulcanized rubber domains. The remaining amount of oil was able to separate as submicron pools distributed in the PP matrix. This caused lowering of T_g, T_m, crystallinity of PP phase as well as strength, elastomeric, and dynamic properties of the TPVs. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 540–548, 2010

Key words: natural rubber (NR); polypropylene; paraffinic oil; degree of crystallinity; glass transition temperature; dynamic properties; mechanical properties; morphological properties

INTRODUCTION

Thermoplastic elastomers (TPEs) combine the elastic and mechanical properties of vulcanized rubber with the processing characteristics of thermoplastic polymer.[1] An important class of TPEs is thermoplastic vulcanizates (TPVs) which has been a fast growing segment of the rubber market. TPVs are produced by dynamic vulcanization of blends containing thermoplastic and an elastomer.[2,3] During preparation of the TPVs, the rubber and thermoplastic are thoroughly mixed in the melting state with the rubber is selectively cured during intensive mixing. Thermoset rubber is then formed by the action of the rubber curative. Shearing at high temperature causes the rubber to break up into 1–5 μm of the dispersed domains.[4] Commercial TPVs are generally produced from isotactic polypropylene (PP) blended with ethylene-propylene diene rubber (EPDM) and

extender oil using a phenolic (i.e., resol) curing system.[5] In addition, various additives such as fillers (carbon black, talcum or clay), stabilizers, pigments, etc. may be added to tailor the properties.[6]

Processing oil is a well-known additive that lowers the hardness and improves the prcessability of TPVs. The PP/EPDM TPVs and PP/SEBS blends can be largely extended with paraffinic oil. Due to the small polarity differences between the three components, the oil can be present in both PP and in elastomer phase.[7] The addition of oil in combination with crosslinking of the rubber phase allows the production of soft compositions with good processability and elastic recovery.[6] Soft TPVs are commercially available with 45 shore A indentation hardness and compression sets approaching values of common thermoset rubbers, while the PP matrix in the TPV allows good thermoplastic properties.[8] The PP phase solidifies and partly crystallizes while the rubber phase remains as discrete small particles dispersed in the PP phase. In the rubbery state, the oil is generally believed to be predominantly absorbed by the EPDM phase. The remaining oil dissolves in the amorphous phase of PP.[9] During deformation in a solid state, elastic behavior arises from both the rubber particles and PP layers surrounding the particles,

which explains the macroscopic elastic behavior.[10] However, in the melting state during mixing and fabricating, the oil is probably distributed into both the PP and rubber phases and results in the ease of processability. Therefore, the addition of low molecular weight processing oil plasticizes both the PP and elastomer phases[9,11,12] and results in reduction of the glass transition temperature (T_gs) of both phases.[7]

TPVs based on natural rubber (NR) and thermoplastic blends [or thermoplastic natural rubber, (TPNR)] are also one of the interesting materials. They typically exhibit the superior mechanical and cure properties of NR. Some studies on TPVs based on blending of NR and PP have been reported.[13–19] The NR/PP TPVs developed by the Malaysian Rubber Producers' Research Association could replace vulcanized rubber in end products where high resilience and strength were not essential but good low temperature performance was needed.[19] They could also replace flexible plastics such as plasticized PVC, ethylene vinyl acetate and PP copolymers.[20] Not only raw NR has been used to prepare TPNRs, but also modified forms have been widely studied. Epoxidized natural rubber is one of the most recognized forms. It has been used to prepare TPNRs by blending with various thermoplastics such as PP,[21–24] poly(vinyl chloride)[25] and poly(methyl methacrylate).[26] In recent years, attempts were made to prepare TPNRs based on maleated natural rubber (MNR) and PP blends via a dynamic vulcanization process. The effect of blend ratios on rheological, mechanical and morphological properties of the MNR/PP TPVs has been investigated.[27] Furthermore, rheological, thermal and morphological properties of reactive blending based on MNR and PMMA have also been described.[28] Among the TPVs based on NR blended with thermoplastics, there are no studies of the effect on properties of the product by the process or extender oil.

In the present work, we examined the influence of paraffinic oil on various properties of the dynamically cured NR/PP TPVs. Mechanical, dynamic, morphological, and thermal properties of the NR/PP TPVs with various loading levels of oil were studied. Trends of glass transition temperature (T_g), crystalline melting temperature (T_m) and degree of crystallinity of the PP phase were correlated with morphological, mechanical, and dynamic properties of the TPVs.

EXPERIMENTAL

Materials

The NR used as a rubber blend component was air-dried sheet (ADS), manufactured by a local factory operated by Khun Pan Tae Farmer Co-operation (Phattalung, Thailand). The PP used as a thermoplastic blend component was an isotactic PP, injection molding grade MD with MFI of 12 g/10min at 230°C and specific gravity of 0.91, manufactured by the Thai Polypropylene Co., Rayong, Thailand. The phenolic resins: dimethylol phenolic resin or octylphenol-formaldehyde resin (SP-1045) used as a reactant to prepare phenolic modified polypropylene (Ph-PP) compatibilizer, were manufactured by Schenectady International, New Port . The blend compatibilizer Ph-PP was prepared in-house as per a procedure described elsewhere.[23] Another type of the phenolic resin with active hydroxymethyl (methylol) groups (HRJ-10518) used as a curing agent for rubber was also manufactured by Schenectady International Inc. Stannous chloride, used as a catalyst in the phenolic curing system and preparation of the Ph-PP compatibilizer, was manufactured by Fluka Chemie (Buchs, Switzerland). The processing oil used in NR/PP TPVs was Sunpar paraffinic oil manufactured by Sunoco Lubricants, Co. The polyphenolic additive, Wingstay® L, used as an antioxidant, was manufactured by Eliokem Inc. (OH).

Preparation of dynamically cured 60/40 MNR/PP TPVs

The oil extended natural rubber (OENR) was first prepared by mixing the NR and paraffinic oil in a dispersion kneader with a mixing chamber of 3 L. (Yong Fong Machinery Co., Samutsakorn, Thailand). The NR (ADS) was first masticated for 3 min at 80°C. Paraffinic oil at a given loading level was then incorporated into the mixing chamber and mixing was continued for 20 min. The mixed product (OENR) was later sheeted out using a two-roll mill. The OENR was then compounded using a two-roll mill at room temperature and the compounding formulation and mixing schedule shown in Tables I and II, respectively. The 60/40 NR/PP TPVs were then prepared via dynamic vulcanization during melt mixing using a Brabender Plasticorder at 180°C and a rotor speed of 60 rpm using the following

TABLE I
Compounding Formulations

Ingredients	Quantity (phr)				
	0[a]	10[a]	20[a]	30[a]	40[a]
NR (ADS)	100	100	100	100	100
Paraffinic oil	–	10	20	30	40
ZnO	5	5	5	5	5
Stearic acid	1	1	1	1	1
Wing stay L	1	1	1	1	1
SnCl$_2$.2H$_2$O	0.6	0.6	0.6	0.6	0.6
HRJ-10518	5	5	5	5	5

[a] Loading level of oil.

Mixing step	Mixing schedule (min)
ADS + paraffinic oil (OENR)	2
ZnO	2
Stearic acid	2
Wing stay L	1
$SnCl_2.2H_2O$	2
HRJ-10518	2
Compound finishing	1

procedure. 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 % of PP was incorporated and mixed for 1 min. The OENR compound was added and mixing was continued until a plateau mixing torque was reached. The blend products were finally pelletized. OENRs with four levels of paraffinic oil at 10, 20, 30, and 40 phr were each studied and compared with the NR without oil (i.e., 0 phr) Mechanical, dynamic, rheological, thermal, and morphological properties of the NR/PP TPVs were characterized.

Preparation of PP blended with paraffinic oil

Various loading levels of paraffinic oil (i.e., 10, 20, 30, and 40 phr) was blended with PP using a Brabender Plasticorder at 180°C and a rotor speed of 60 rpm. The PP was first preheated for 6 min in the mixing chamber without rotation and it was then melted for 2 min at a rotor speed of 60 rpm. The paraffinic oil was then incorporated and mixed for another 5 min. The oil extended PP was then cooled down to room temperature and left over night before characterizing the thermal properties.

Mechanical testing

Tensile testing of the TPV 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 Co., UK. The dumbbell shaped specimens, 2 mm thick, were prepared by a thermoplastic injection molding machine with a clamping force capacity of 90 tons (Welltec Machinery), Hong Kong. Tension set at 100% elongation was also determined at room temperature (25°C ± 2°C) according to ISO 2285. The samples were kept under tension for a fixed elongation and time interval then they were released from the clamp, set aside for another fixed time interval and then the changes in the sample dimensions were determined. Hardness of the samples was also measured using indentation shore A, according to ISO 7619.

Dynamic properties

Dynamic properties of 60/40 NR/PP TPVs were characterized using a rotorless oscillating shear rheometer (RheoTech MDPT, Cuyahoya Falls) at 180°C. The oscillation frequency was set in the range of 1 to 30 Hz at a constant strain of 3%. This was to assure that the test was in the range of linear viscoelasticity. The storage (G') and loss shear (G'') moduli, loss factor, $\tan \delta = G''/G'$ and the complex viscosity (i.e., $\eta^* = G^*/\omega = \eta'' + i\eta'$) of the TPVs were characterized.

Thermal property characterization

Differential scanning calorimetry (DSC, TA Instruments, TX) was used to follow the thermal behavior of the dynamically cured 60/40 NR/PP TPVs with various loading levels of paraffinic oil compared with the pure NR and PP. The oil extended PP with various loading of oil was also characterized. The DSC was performed with the instrument under nitrogen atmosphere. The samples were first heated to 200°C, maintained at that temperature for 5 min to eliminate any thermal history. The sample was then quenched to –120°C at a cooling rate of 10°C/min. Thereafter, the specimens were heated again at a heating rate of 10°C /min until 200°C. The glass transition temperature, T_g, of the samples were determined from the midpoint of the transition. Also, the degree of crystallinity of PP phase, X_{PP}, was calculated based on the heat of crystallization of the blend, ΔH_{TPV}, the heat of crystallization of PP, ΔH_{PP} (= 209 J/g)[29] and its mass fraction, m_{PP}:

$$X_{PP} = \frac{\Delta H_{TPV}}{m_{PP}\Delta H_{PP}} \tag{1}$$

Morphological studies

Morphological studies were carried out using a Leo scanning electron microscope, model VP 1450, manufactured by Leo Co., Cambridge, UK. Molded samples of the thermoplastic vulcanizates were cryogenically cracked in liquid nitrogen to avoid any possibility of phase deformation. The PP phase was preferentially 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

Mechanical and morphological properties

Figure 1 shows stress-strain curves of dynamically cured 60/40 NR/PP blend with different loading levels of paffinic oil. The interfacial adhesion
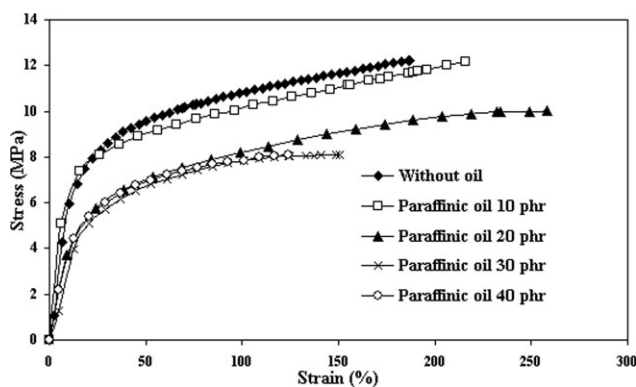
Figure 1 Stress-strain curves of dynamically cured 60/40 NR/PP with various loading leves of paraffinic oil.

Figure 2 Hardness of dynamically cured 60/40 NR/PP with various loading level of paraffinic oil.

between PP and rubber phases was promoted by compatibilizing effect of phenolic modified PP (Ph-PP) compatibilizer which is capable of forming block copolymer of PP and NR.[30] Each block of the copolymer could interact with the corresponded blend component. Therefore, higher mechanical strength and smaller dispersed vulcanized rubber domains were observed.[30] In this work, the Ph-PP compatibilized blends were also prepared to visualize the influence of oil content on various properties of the blends. In Figure 1, it is seen that the slope at initial linear region of the curves (i.e., Young's modulus) gradually decreased with an increasing loading level of oil. This indicates lower stiffness of the material with increasing oil content. Furthermore, it is clear that the TPVs with moderate loading levels of oil (i.e., 10 and 20 phr) exhibited higher extension at the failure position. This is confirmed by the elongation at break of the TPVs with various loading levels of the paraffinic oil, as shown in Figure 1. That is, an increasing loading level of oil in a range of 0–20 phr caused increasing elongation at break of the TPVs. However, increasing the content of oil higher than 20 phr, abruptly decreased the trend of the elongation at break. The increase in elongation at break of the TPVs in a range of oil 0 to 20 phr is attributed to the distribution of oil into both PP and vulcanized domains of NR phases. This caused dissolving of the crystalline phase in PP and plasticizing or swelling of the NR phase. Therefore, higher amorphous content in the PP phase and softer NR domains were a consequence. The material then showed greater extensibility without rupture. However, with incorporation of paraffinic oil higher than 20 phr a decreasing trend of elongation at break was observed. This is attributed to the quantities of oil incorporated being above the optimum level and causing the excess amount of oil to form a separate oil phase or oil domain in the PP matrix. This would cause a weak point and failure upon tensile testing and lower extensibility.
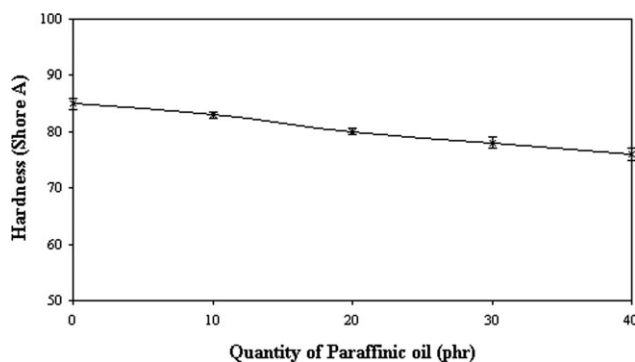
Figures 1 and 2 show tensile strength and hardness of the 60/40 NR/PP TPVs mixed with various loading levels of the paraffinic oil, respectively. As expected, the strength and hardness properties of the TPVs decreased with increasing loading levels of oil. This is due to diffusion of the oil and dissolving of the crystalline phase in the PP and plasticizing of the NR phase. Therefore, the amount of oil in TPVs could be used to adjust or specify hardness or strength properties for manufacturing various grades of the material for different industrial applications. It is important to note that while increased loading levels of oil caused inferior tensile and hardness properties, the oil extended TPVs exhibited ease of processability. They could be easily fabricated by plastic injection molding with low injection pressure and lower melt viscosity than that of the ones without oil.

Figure 3 shows tension set properties of the dynamically cured NR/PP TPVs with various loading levels of paraffinic oil. The TPV with a content of oil at 20 phr exhibited the lowest value of tension set or the highest elastomeric nature (i.e., rubber elasticity). We verified this phenomenon by using SEM micrographs, as shown in Figure 4. It can be seen that the NR/PP TPVs exhibited phase separation with the micron size vulcanized rubber domains dispersed in the PP matrix. Furthermore, the TPV
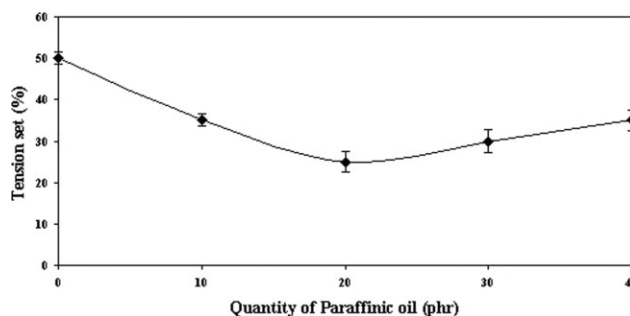

Figure 3 Tension set of dynamically cured 60/40 NR/PP with various loading level of paraffinic oil.
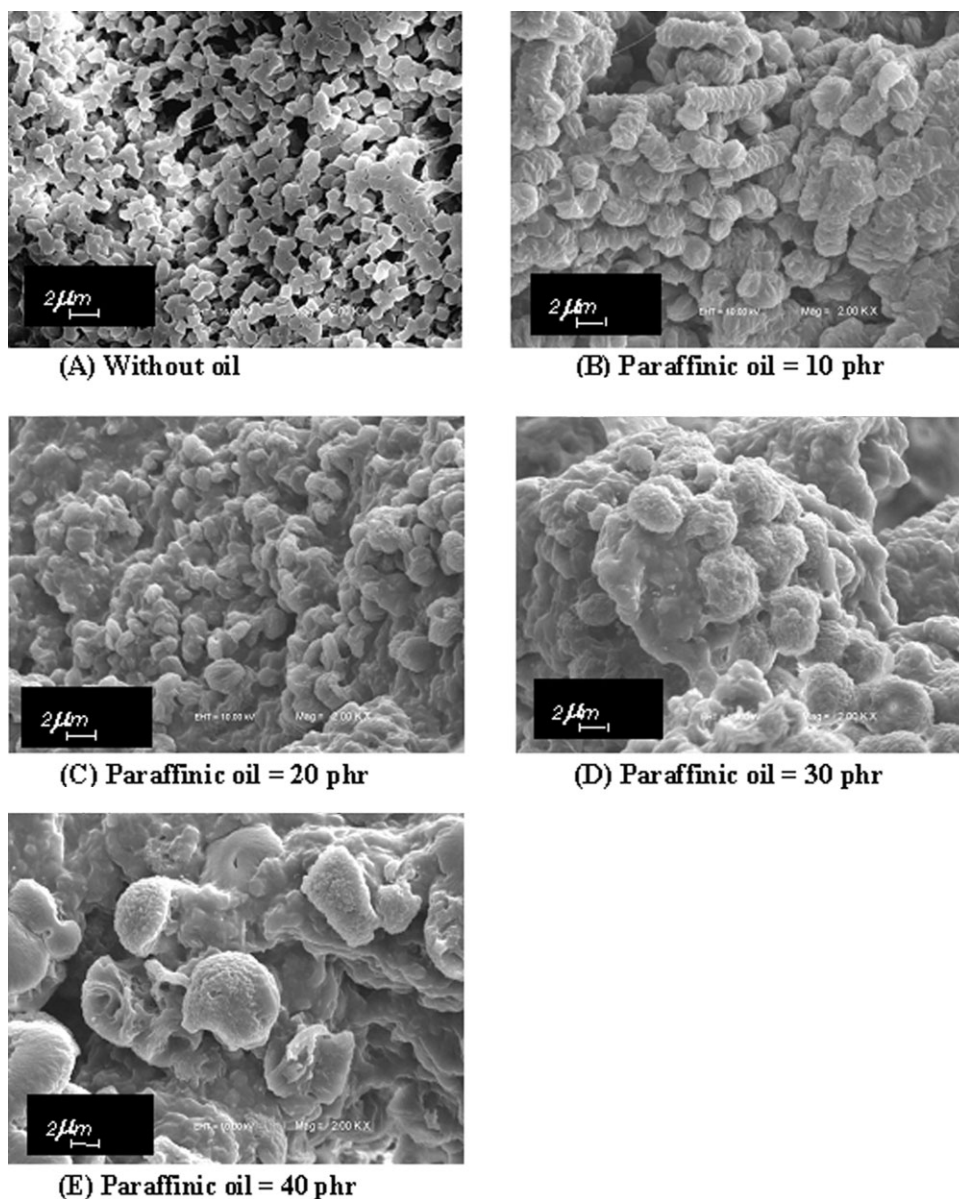
Figure 4 SEM micrographs of dynamically cured 60/40 NR/PP with various loading levels of paraffinic oil.

without oil showed the smallest dispersed vulcanized rubber domains (i.e., smaller than 1 μm). Incorporation of oil caused distribution of oil into PP and vulcanized rubber phase, as mentioned earlier. As a consequence, higher amorphous region (or lower crystalline phase) in the PP and larger swollen vulcanized rubber domains were observed. In Figure 4(B,C), the TPVs with 10 and 20 phr of oil, size of vulcanized rubber domains are slightly larger those without oil. This is presumably due to a low level of oil diffusing and swelling in the rubber domains. Therefore, at these loading levels of oil, a major part of the oil might diffuse into the PP phase because of more structural similarity. This would cause dissolving of the crystalline phase and turn it into a miscible component, oil-swollen amorphous region. As a

result, higher elongation at break because of the greater extension of amorphous phase, as evidenced in Figure 1 would occur. However, increasing loading levels of oil higher than 20 phr caused saturation of oil in the PP phase. Therefore, a higher proportion of oil might diffuse into the vulcanized NR domains and increase the degree of swelling of the domains, or oil-swollen rubber phase, as seen in Figure 4(D,E) for the TPVs with 30 and 40 phr of oil. It is clear that the oil-swollen rubber domains are larger with the domain size ~2 μm or more. The remainder of the oil was present as a separate phase that consisted of submicron pools of oil distributed in the PP matrix.[4] However, this observation did not agree with PP/EPDM TPVs where the oil was predominantly absorbed by the EPDM phase.[9]
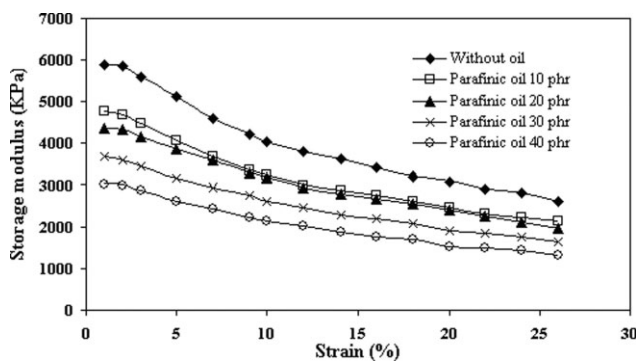
Figure 5 Storage modulus as a function of strain of dynamically cured 60/40 NR/PP with various loading level of paraffinic oil, tested at 180°C and frequency of 1 Hz.

Dynamic properties

Figure 5 shows storage modulus as a function of strain amplitude of dynamically cured 60/40 NR/PP with various loading levels of paraffinic oil. It can be seen that the storage modulus reached a linear region at a strain amplitude lower than 3%. For the storage modulus at a given strain amplitude, it can be seen that the G' of the TPV without oil showed the highest value. Increasing loading levels of oil caused decreasing level of G'. However, the G' of the TPVs with 10 and 20 phr of oil showed very similar values. This might be related to the similar size of phase morphology shown in Figure 4(B,C). That is, decreasing trend of elastic response of the material was observed with increasing oil content. However, the ratio between G'' and G' (i.e., tan δ) of the TPV with 20 phr of oil (Fig. 6) exhibited the lowest value. This reveals that this type of material exhibited the lowest viscous response but very high elastic response. This result corresponds to the level of tension set in Figure 3 where the material with 20 phr of oil exhibited the lowest tension set value or the highest elatomeric properties.

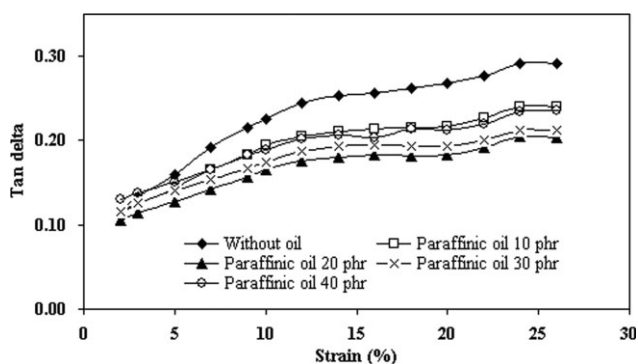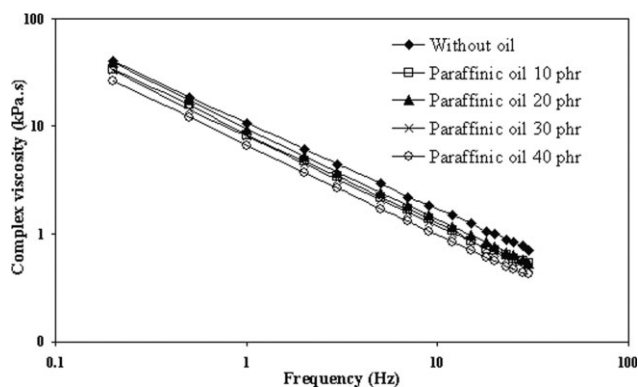Figure 7 shows complex viscosity as a function of frequency of dynamically cured 60/40 NR/PP TPVs

Figure 7 Complex viscosity as a function of frequency of dynamically cured 60/40 NR/PP with various loading level of paraffinic oil and tested at 180°C.

with different loading levels of oil. It is clear that the complex viscosity decreased with increasing oscillating frequency (or shear rate). This confirms the shear thinning behavior for this type of TPV. At a given frequency, it is seen that the complex viscosity decreased with increased loading levels of the oil. This is attributed to the oil behaving as an internal lubricant to promote the ease with which molecules slide pass each other. As a result, lower flow resistance was observed. This is a very important criteria for the fabrication process of the TPV. That is, a lower injection pressure and temperature would be possible for fabricating of the TPVs. The ease of processability was also observed in the case of EPDM/PP TPVs upon incorporation of the process oil.[7]

Thermal properties

Figure 8 shows DSC thermograms of dynamically cured 60/40 NR/PP with various loading levels of

Figure 6 Tan δ as a function of strain of dynamically cured 60/40 NR/PP with various loading levels of paraffinic oil and tested at 180°C.
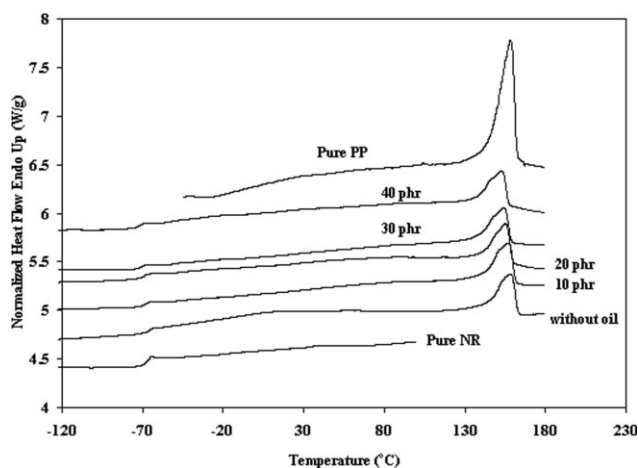

Figure 8 DSC thermograms of dynamically cured 60/40 NR/PP with various loading levels of paraffinic oil compared with pure NR and PP.
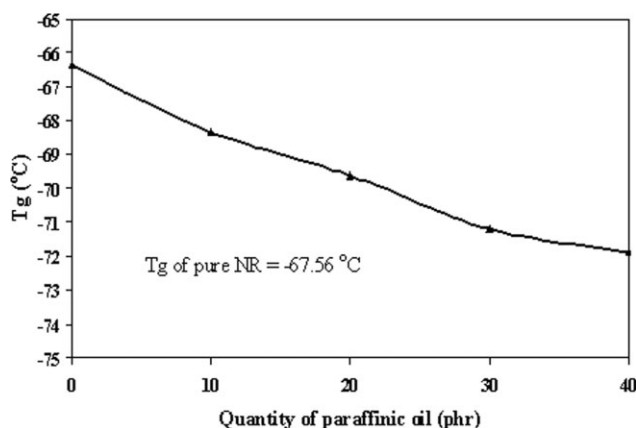
Figure 9 Glass transition temperature (T_g) of dynamically cured 60/40 NR/PP with various loading level of paraffinic oil compared with pure NR and PP.

paraffinic oil compared with pure NR and PP, respectively. It is seen that the glass transition temperature (T_g) of the rubber phase was clearly observed at low temperature ranges. Furthermore, the crystalline melting temperature (T_m) of the PP phase was also observed. However, the glass transition temperature of the PP phase could not be determined by this technique. Decreasing trend of T_g was observed upon increased loading level of oil, as shown in Figure 9. This is attributed to distribution of oil into the dispersed vulcanized rubber domains causing an oil-swollen rubber phase. Therefore, the rubber chains gain greater flexibility and a lowering of the T_g. The results agree with the previous observations in EPDM/PP TPVs.[4,7] This would give higher elastomeric properties with increased loading levels of oil. However, the TPVs are two-phase systems consist of elastomer and thermoplastic. The properties of the PP matrix has to be taken into account. More incorporated oil caused lower strength properties of the PP and they were more extendable in particular at loading levels of oil higher than 20 phr. This is a result of distribution of oil into PP matrix, as evidence in DSC thermograms
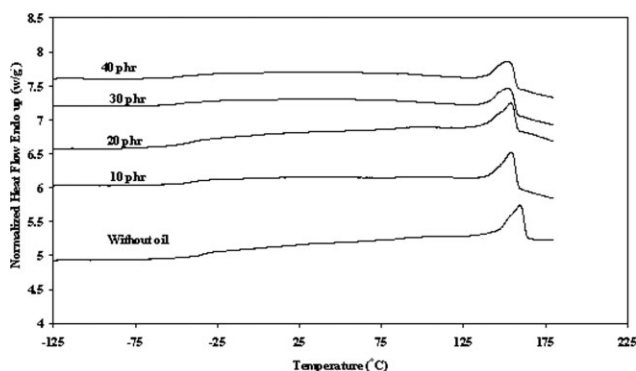

Figure 10 DSC thermograms of pure PP with various loading levels of paraffinic oil.

TABLE III
Degree of Crystalinity of Pure PP and PP in 60/40 NR/PP TPVs

Quantity of paraffinic oil (phr)	Degree of crystalinity (%)	
	Pure PP	60/40 NR/PP TPVs
0	51.80	28.00
10	47.12	25.33
20	39.08	19.97
30	38.11	18.91
40	37.21	17.67

of pure PP with various loading levels of oil in Figure 10. It clear seen that increasing loading levels of oil in the PP caused lowering of T_m and area under the melting curves or the degree of crystallinity.

Table III and Figure 11 shows degree of crystallinity of the PP (X_{PP}) phase in dynamically cured NR/PP (based on the DSC thermograms in Fig. 8) and of the pure PP with various loading levels of oil (based on the DSC thermograms in Fig. 10). It is clear that the X_{PP} shows decreasing trend with increasing oil contents. Abrupt decreasing trend of X_{PP} was observed in a range of oil 0 to 20 phr and thereafter the marginal decreasing trend was observed. In Figure 11, it is clear that the degree of crystallinity of PP phase in TPVs exhibited a large difference compared with the crystallinity of the pure PP. That is, the degree of crystallinity of the TPV without oil is 28.01% while the value for the pure PP is 51.80%. This is attributed to incorporation of various blends components at mixing conditions with high temperature and shearing action. This caused the disappearance of some parts of the regular region of PP molecules and the appearance of an irregular amorphous phase. It is also seen that in the pure PP the oil caused lowering of the crystalline phase in particular at a loading of oil in the range 0 to 20 phr. In Figure 11, it is also seen that the abrupt decreasing
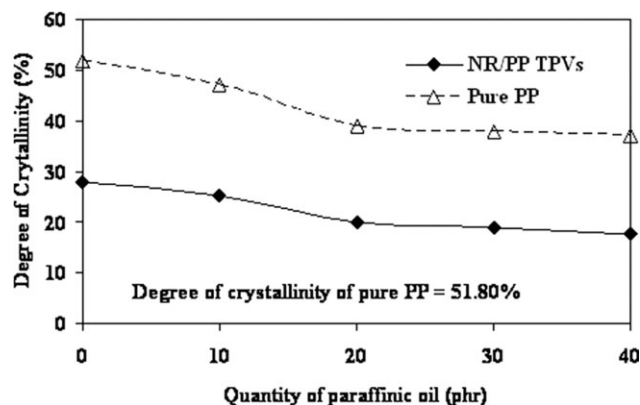

Figure 11 Degree of crystallinity of PP phase of dynamically cured 60/40 NR/PP and pure PP with various loading level of paraffinic oil.
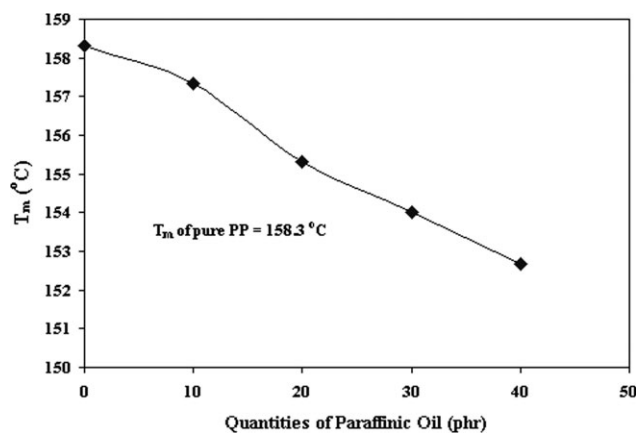
Figure 12 Crystalline melting temperature (T_m) of dynamically cured 60/40 NR/PP with various loading level of paraffinic oil compared with pure NR and PP.

trend of the degree of crystallinity was observed for the TPVs with oil in a range of 0–20 phr. This confirms our previous hypothesis that the oil might prefer to diffuse toward the PP phase at these loading levels of oil and cause an abrupt decreasing trend of the degree of crystallinity and hence a higher level of oil-swollen amorphous phase. Therefore, a lower proportion of oil would be available to distribute into the rubber phase and cause less swelling of the vulcanized rubber domains in the TPVs, as evidences in Figure 4(B,C). In Figure 11, increasing loading levels of oil in the TPVs to higher than 20 phr resulted in marginally decreasing trend of the degree of crystallinity. In this case, the oil in the PP phase might approach a saturation state and excess oil might be forced to diffuse into the rubber phase. This will result in larger swollen vulcanized rubber domains dispersed in the PP matrix, as seen in Figure 4(D,E). Therefore, for the whole range of oil used, increasing loading levels of oil in the TPVs resulted in decreasing of degree of crystallinity or increasing of amorphous phase of the PP. As a result, decreasing trend of strength properties (Fig. 1), hardness (Fig. 2), storage modulus (Fig. 5) and complex viscosity (Fig. 7) was observed. Increasing oil content also influenced crystalline melting temperature (T_m), as shown in Figure 12. That is, the T_m of TPVs decreased with increasing loading levels of oil. Therefore, the lower level of crystallinity in the PP phase could be melted at a lower temperature.

CONCLUSIONS

Dynamically cured 60/40 NR/PP blends with the phenolic cured system and phenolic modified PP (Ph-PP) compatibilizer were prepared with loading levels of paraffinic oil at 0, 10, 20, 30, and 40 phr. Influence of loading levels of oil on mechanical, dynamic, thermal and morphological properties of

the TPVs was investigated. It was found that stiffness, hardness, tensile strength, storage shear modulus (G') and complex viscosity (η^*) of the TPVs decreased with increasing loading level of oil. Furthermore, increasing loading of oil caused decreasing trend of T_g of the vulcanized rubber phase, degree of crystallinity and T_m of the PP phase. This is attributed to distribution of oil into the PP and vulcanized rubber domains causing oil-swollen amorphous phase in the PP and oil-swollen vulcanized rubber domains, respectively. It is anticipated that amount of oil could be used to adjust hardness and other related properties of the TPVs. It was also found that the TPVs with oil in a range of 0–20 phr exhibited increasing trend of elongation at break and elastic response in term of tension set and damping factor (tan δ). This is ascribed to the major proportion of oil being first preferably migrated and diffused into the PP phase because of structural similarity. This caused an abrupt decreasing trend in degree of crystallinity and T_m of the PP phase. On the other hand, the micron size of dispersed vulcanized rubber domains of the TPVs with 10 and 20 phr of oil showed small particles with low degree of swelling. Therefore, high interfacial adhesion between different phases caused higher elongation at break and elastic response. Increased loading of oil higher than 20 phr caused decreasing trend of elongation at break, elastomeric properties and all other properties investigated. This is due to oil saturation in the PP phase and creation of larger swollen vulcanized rubber domains. Also, the excess amount of oil was present as a separate oil phase that consisted of submicron pools of oil distributed in the PP matrix which behaved as a weak point that failed upon deformation.

References

1. Holden, G.; Legge, N. R., Eds. Thermoplastic Elastomers; Hanser Publishers: New York, 1996.
2. Coran, A. Y.; Patel, R. P. Rubber Chem Technol 2006, 53, 141.
3. Coran, A. Y. Handbook of Elastomers-New Development and Technology; Bromwick, A. K., Stephan, H. L., Eds.; Marcel Dekker: New York, 1992.
4. Abrahim, T.; Barber, N. G.; Mallamaci, M. P. Rubber Chem Technol 2007, 80, 324.
5. Van Duin, M.; Souphanthong, A. Rubber Chem Technol 1995, 68, 717.
6. Winters, R.; Lugtenburg, J.; Litvinov, V. M.; Van Duin, M.; De Groot, H. J. M. Polymer 2001, 42, 9745.
7. Sengers, W. G. F.; Wübbenhorst, M.; Picken, S. J.; Gotsis, A. D. Polymer 2005, 46, 6391.
8. Coran, A. Y. Thermoplastic Elastomers—A Comprehesive Review; Legge, N. R.; Holden, G.; Schroeder, H. E., Eds.; Hanser Publishers: New York, 1992.
9. Ellul, M. D. Rubber Chem Technol 1998, 71, 144.
10. Kawabata, S.; Kitawaki, S.; Arisawa, H.; Yamashita, Y.; Guo, X. J Appl Polym Sci: Appl Polym Symp 1992, 50, 245.

11. Ohlsson, B.; Hassander, H.; Tornell, B. Polym Eng Sci 1991, 36, 501.
12. Vennemann, N.; Hundorf, J.; Kummerlowe, C.; Schulz, P. Kautsch Gummi Kunstat 2001, 54, 362.
13. Elliott, D. J.; Tinker, A. J. Ind Della Gomma 1987, 31, 30.
14. Teh, J. W.; Tan, L. C.; Chia, C. T.; Tan, K. K.; Teng, T. T. Structure, processing and mechanical behavior of polypropylene-natural rubber blends. In Proceedings of the Composites Asia Pacific 89 Conference; Adelaida, June 1989
15. Sain, M. M.; Simek, I.; Beniska, J.; Rosner, P. J Polym Mater 1990, 7, 49.
16. Cook, S.; Tinker, A. J.; Patel, J. WO Pat. application 03/054078 A1, 2003.
17. Karmika, G.; Rangith, S. L. G.; Warnapura, S. S.; Abeysekera, W. P. M. Some aspects of rheological characteristics of natural rubber and polypropylene blends. In Proceedings of the Conference of Natural Rubber: Current Developments in Product Manufacture and Applications; Kuala Lumpur, June 1993.
18. Kuriakose, B.; De, S. K. Polym Eng Sci 2004, 25, 630.
19. Tinker, A. J. Polym Commun 1984, 25, 325.
20. Varghese, S.; Alex, R.; Kuriakose, B. J Appl Polym Sci 2004, 92, 2063.
21. Nakason, C.; Wannavilai, P.; Kaesaman, A. J Appl Polym Sc 2006, 100, 4729.
22. Nakason, C.; Wannavilai, P.; Kaesaman, A. J Appl Polym Sc 2006, 101, 3046.
23. Nakason, C.; Wannavilai, P.; Kaesaman, A. Polym Test 2006, 25, 34.
24. Huang, H.; Yang, L.; Ni, X. J Macromol Sci Phys 2005, 44, 137.
25. Ratnam, C. T.; Nasir, M.; Baharin, A.; Zaman, K. Polym Deg Stab 2001, 72, 147.
26. Nakason, C.; Toprakhon, A.; Kaesaman, A. J Appl Polym Sc 2005, 98, 1251.
27. Nakason, C.; Saiwari, S.; Kaesman, A. Polym Eng Sci 2006, 46, 594.
28. Nakason, C.; Saiwari, S.; Tatun, S.; Kaesman, A. Polym Test 2006, 25, 656.
29. Brandrup, J.; Immergut, E. H.; Grulke, E. A. Polymer Handbook; Wiley: London, 1999.
30. Nakason, C.; Saiwari, S. J Appl Polym Sc 2008, 110, 4071.