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Novel thermoplastic vulcanizates based on polyamide 12 blends: influence of modified devulcanized natural rubber gloves on properties of the blends

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Abstract

Alternative application for utilization of recycled rubber is extended in thermoplastic elastomer. Thermoplastic vulcanizates (TPVs) from blends of polyamide 12 (PA 12) and devulcanized rubber from waste of natural rubber gloves (DNRG) have been successfully prepared. The TPVs remarkably exhibit superior elasticity compared to the original PA 12. Further improvement of physical properties of the TPVs has been elaborated by introducing maleated DNRG (MDNRG). The grafting efficiency of maleic anhydride onto the MDNRG backbone was confirmed by FTIR technique. The MDNRG/PA 12 TPVs exhibited greater stiffness and damping factor compared to the DNRG/PA 12 TPVs. This is attributed to chemical interaction between polar functional groups in the PA 12 molecules and anhydride groups in the MDNRG molecules which have been proved by ATR-FTIR and TSSR techniques. Moreover, the interfacial interaction facilitates higher interfacial adhesion between the both phases consequently results in the significant improvement of the MDNRG/PA 12 TPVs mechanical and elastic properties. This is in good agreement to the morphology of the blends. It is verified that the smaller micron-sized vulcanized rubber domains dispersed in the PA 12 matrix is found in the MDNRG/PA 12 TPVs compared to the DNRG/PA 12 TPVs.

1. Introduction

Thermoplastic elastomers (TPEs) are elastomeric materials that can be processed using thermoplastic processing equipment. They are commonly defined as the materials that combine properties of hard thermoplastics and soft elastomers. The TPE materials have gained more importance nowadays due to the wide range of applications in fields such as automotive parts, house hold appliances, electrical equipment, industrial supplies and medical applications [1]. However, most commercially available TPEs are manufactured from nonrenewable petrochemical polymers. With increasing anxiousness of environmental issue and fuel shortage in the future, natural rubber and other renewable and sustainable resources are decidedly the coming materials in the future uses. One of these attractive resources used in preparation of TPE is recycled natural rubber because the ease of processing, its appropriate elastomeric properties, and low cost.

TPE prepared from blending of recycled natural rubber and thermoplastic have been comprehensive studied [2-4]. However, it is well known that natural rubber has poor weathering resistance as well as poor oils and chemicals resistance. Moreover, in preparation of TPE, the natural rubber shows incompatibility with polar thermoplastics [5]. Therefore, chemical modification of natural rubber molecules is probably a route to improve the inferior properties of natural rubber. It is obvious that improvement of thermal properties was observed in the modified natural rubber including in the form of epoxidized natural rubber (ENR) [6, 7], maleated natural rubber (MNR) [8, 9], halogenated natural rubber (HNR) [10] graft copolymers of natural rubber with vinyl monomers (i.e., styrene) [11] or methyl methacrylate (MMA) [12] and natural rubber grafted with phosphate functional group [13]. Furthermore, the chemically modified natural rubber molecules have been used to enhance the blend compatibility with various types of polar polymers [12, 14, 15].

In this work, an attempt was made to prepare maleated devulcanized natural rubber gloves (MDNRG). The MDNRG was then used to prepare TPVs by blending with polyamide 12 (PA 12). Polyamide (PA) has been applied in a wide range of engineering applications as its excellent oil and weather resistance, and high mechanical strength. Therefore, blending of PA and modified recycled natural rubber could provide the materials with higher mechanical, good elasticity and better damping properties. The TPVs have been prepared *via* a dynamic vulcanization technique with a fixed blend ratio of MDNRG/PA 12 = 50/50 wt%. The DNRG/PA 12 TPVs was also prepared for comparison purposes. To date, no detailed investigation concerning the use of these materials to prepare TPVs have been available. Mechanical, stress relaxation, dynamic and morphological properties of the blend were investigated. The chemical interaction between devulcanized rubber and PA 12 phases was

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characterized using Fourier transform infrared spectroscopy (FTIR) and temperature scanning stress relaxation (TSSR) technique.

2. Experimental

2.1 Materials

2.1.1 Devulcanized natural rubber gloves (DNRG)

Thermo-chemical de-vulcanization method was used to prepare the devulcanized rubber (DR) from natural rubber gloves. The DNRG was prepared by devulcanzation in internal mixer at 170°C with the devulcanizing time of 5 min using treated distillate aromatic extract oil (TDAE) (5 phr) as devulcanization oils and diphenyl disulfide (DPDS) (1 phr) as devulcanization aids.

2.1.2 Polyamide 12 (PA 12)

Thermoplastic component of this work was injection molding grade of PA 12 (Grilamid L20G). Grilamid L20G with density of 1.01 g·cm^{-3}, melting temperature of 178°C, and melt flow rate of 125 g/10 min (275°C/5 kg) was purchased from EMS-Grivory GmbH, Gross-Umstadt, Germany.

2.1.3 Other chemicals

Maleic anhydride was employed to prepare MDNRG, manufactured by Sigma-Aldrich Co, Ltd., Dorset, England. An antioxidant used at loading level of 1 phr was N'-phenyl-p-phenylenediamine (6PPD) while a vulcanizing agent at loading level of 14 phr used in this work was phenolic resin (i.e., HRJ-10518).

2.2 Preparation of MDNRG

MDNRG was prepared *via* melt blending process by mixing 100 phr of DNRG with 8 phr of maleic anhydride in the internal mixer at 135°C for 10 min [8,16]. The obtained product was then purified by re-precipitation method by first dissolving a MDNRG product in toluene at room temperature for 24 h. After that the dissolved MDNRG was boiled at 60°C for 2h. This process was repeated to ensure that all un-reacted MA was removed. The MDNRG solution was later filtered. Thereafter the filtrate product was precipitated, separated and washed thoroughly with acetone. Finally, the purified product was dried in a vacuum oven at 40°C for 24 h. FTIR (Bruker Tensor27, Bruker Corporation, Massachusetts, USA) was used to characterize the purified product.

2.3 Preparation of dynamically cured DNRG/PA 12 and MDNRG/PA 12 blends

Two mixing steps was used to prepare the dynamically cured DNRG/PA 12 and MDNRG/PA 12 blends or TPVs. Firstly, compounding the devulcanized rubbers (i.e., DNRG and MDNRG) was performed in an internal mixer (Brabender® GmbH & Co.KG, Duisburg, Germany) at 60°C for 5 min. Table 1 represented the compounding recipe and mixing schedule of DNRG/ MDNRG. The DNRG and MDNRG compounds were stored at ambient temperature for minimum 3 h prior to prepare dynamically cured DNRG/PA 12 and MDNRG/PA 12 blends. Secondly, the 50/50 w/w of DNRG/PA 12 or MDNRG/PA 12 TPVs was prepared by melt blending in the internal mixer at 180°C for 6 min. In this step, the PA 12 was first eliminated moisture by drying in hot air oven for 24 h prior to load into the mixing chamber. The PA 12 was firstly added and melted at 180°C for approximately 2 min and then the DNRG or MDNRG compound was added. The PA 12 and devulcanized rubber were melt-blended for another 4 min or until fully vulcanization of rubber phase, which can be recognized by steady of mixing torque as function of time. The final product was then dumped from the internal mixer. A thin sheet of the TPVs with 2 mm thick was fabricated by using a compression molding at 180°C.

Table 1. Compounding formulation and mixing schedule on using DNRG or MDNRG.

Ingredients	Quantities (phr)	Time (min)
DNRG or MDNRG	134	2
6PPD	1	1
Phenolic resin (HRJ-10518)	14	2

2.4 Testing and characterization

2.4.1 Tensile, tension set and hardness tests

Hounsfield Tensometer, model H 10KS was used to test the mechanical properties i.e., tensile strength and elongation at break of DNRG/PA 12 and MDNRG/PA 12 TPVs in accordance with ASTM D 412 with testing condition at 25±3°C and the crosshead speed of 500 mm/min. Tension set at 100% strain was targeting to evaluate the elastic properties of the materials and evaluated at room temperature (ASTM D412) with a fixed strain of 100% for 10 min. Digital hardness tester was selected to evaluate the hardness in Shore A.

2.4.2 Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR)

Interfacial reaction between devulcanized rubber (i.e., DNRG and MDNRG) and PA 12 molecules was elucidated using ATR-FTIR technique by Bruker Tensor 27 (Bruker Corporation, Massachusetts, USA). The PA 12 phase was extracted out from the samples by dissolving in dimethyl sulfoxide solvent. The process was repeated more than twice to remove all unreacted PA 12. The remained rubber fraction was precipitated by using ethanol solvent. Thereafter, the extracted rubber was dried in a vacuum oven at 40°C for 24 h. Interfacial reaction between devulcanized rubber and PA 12 molecules was determined by using ATR-FTIR using the ranges of the wavenumber of 3,500-500 cm^{-1}.

2.4.3 Temperature scanning stress relaxation (TSSR)

Temperature scanning stress relaxation technique (TSSR) was used to confirm interfacial reaction between functionalized devulcanized rubber (i.e., DNRG and MDNRG) and PA 12 molecules in the devulcanized rubber/PA 12 blends [17]. The TSSR measurement was performed using TSSR instrument (Brabender GmbH Duisburg, Germany). During the TSSR test, a constant tensile strain of 50% was applied to a dumbbell-shaped sample (type 5A, ISO527). After applying the initial strain, the sample was pre-conditioned at 23°C for 2 h. The sample was then heated with a constant rate of 2 K·min^{-1} until rupture of the sample. The TSSR measurement provides the force-temperature curves, which the certain characteristic, such as T_{10}, T_{50}, T_{90} and the rubber index (RI) are calculated. The temperatures T_{10}, T_{50} and T_{90} indicate the temperatures which the force has decreased about 10%, 50% and 90% with regarding to F_0 (initial force). Moreover, the rubber like behavior of the material can be captured from the RI value which is calculated based on area under force-temperature curves according to the equation below [18].

$$\mathrm{RI} = \frac{\int_{T_0}^{T_{90}} F(T)/F_0 dT}{T_{90} - T_0} \qquad (1)$$

where $F(T)$ is the force from initial until end of testing temperature T while F_0 indicate the initial force at 23°C (T_0). The T_{90} represents the temperature at 90% drop of the force with regard to initial force (F_0).

2.4.4 Dynamic properties

Dynamic properties were characterized using a rubber process analyzer D-RPA 3000 (MonTech Werkstoffprüfmaschinen GmbH, Buchen, Gremany) at 180°C with oscillation frequencies in the range of 0.05-30 Hz. The constant strain of approximately 7 % was set to assure linear viscoelasticity of the sample during the test. The devulcanized rubber/PA 12 sample was first pre-heated for 5 min at a testing temperature without oscillation and then tested in the frequency range of 0.05-30 Hz. Damping factor (Tan δ) is calculated based on the ratio of loss modulus (G'') to storage modulus (G') of the blends at the test condition.

2.4.5 Morphological characterization

Scanning electron microscope (SEM 5800, Jeol Ltd., Tokyo, Japan) was used to image the morphology of the DNRG/PA 12 TPVs and MDNRG/PA 12 TPVs. Each sample was first cryogenically cracked in liquid nitrogen to prevent any possibility of phase deformation. The fractured surface of sample was immersed into hot dimethyl sulfoxide at 190°C for 10 min to extract the PA 12 phase. The sample was then dried in a vacuum oven at 50°C for 24 h to remove the solvent. After the volatilization of solvent, the dried sample was then gold-coated and characterized by the SEM.

3. Results and discussion

3.1 FTIR characterization of MDNRG

Typical FTIR spectra of DNRG and MDNRG are shown in Figure 1. The wavenumbers and respective assignments are listed in Table 2. It is seen that the DNRG and MDNRG show similar absorption peaks at a wavenumber of 835 and 1660 cm^{-1} which correspond to =C–H out-of-plane bending and –C=C– stretching of natural rubber molecules. The distinct bands observed for the MDNRG over the DNRG are the peaks at wavenumbers of 1854 to 1710 cm^{-1}. This clearly confirms the functional group of maleic anhydride is successfully grafted onto the DNRG backbone.

Table 2. Important absorption peaks of the MDNRG compared with the DNRG.

Wavenumber (cm^{-1})	**Functional groups**	**Types of rubber**	
		DNRG	**MDNRG**
1854	–C=O stretch of succinic anhydride		✓
1784	–C=O stretch of polymeric anhydride		✓
1710, 1736	–C=O stretch, carbonyl group		✓
1660	–C=C stretch of NR	✓	✓
835	=C–H out-of-plane bend of NR	✓	✓

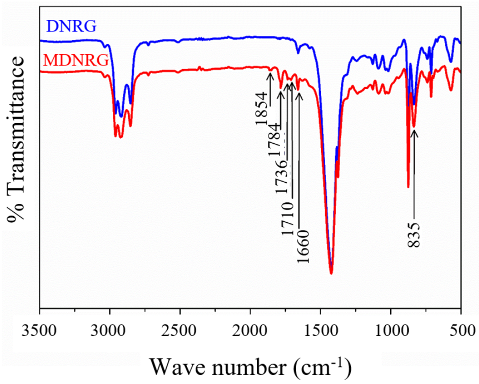

Figure 1. FTIR spectra of the MDNRG compared with the DNRG.

3.2 Mechanical properties, hardness and dynamic properties of the devulcanized rubber/ PA 12 TPVs

Figure 2 shows the stress-strain curves of devulcanized rubber/PA 12 blends containing different types of DNRGs. The curves reveal different deformation nature of pure PA 12 and the TPVs under applied stress. Yielding process was found at around 10% of elongation for pure PA 12, indicating the semi-crystalline plastic in nature of PA 12. When PA 12 was blended with DNRG or MDNRG, the stress-strain behavior has developed from semi-crystalline plastic to elastic type with disappearance of yielding phenomenon. This is due to increasing of elastic proportion in the blends. Comparing between MDNRG/PA 12 and DNRG/PA 12 TPVs, it can be seen that the MDNRG/PA 12 TPVs exhibited higher initial slope at the beginning of the curves (i.e., Young's modulus) than that of the DNRG/PA 12 TPVs. This indicates higher stiffness of MDNRG/PA 12 TPVs which might be attributed to chemical interaction between anhydride groups in MDNRG molecules and polar functional groups of PA 12 (i.e., –NH2, –COOH, –NH–CO–, respectively).

Table 3 shows mechanical properties, hardness and dynamic properties of pure PA 12, DNRG/PA 12 TPVs and MDNRG/PA 12 TPVs. It can be seen that the MDNRG/PA 12 TPVs show superior mechanical properties than that of the DNRG/PA 12 TPVs. This corresponds to the chemical interactions in the modified MDNRG/PA 12 TPVs. Furthermore, it can be seen that both TPVs have exhibited lower hardness than that of the pure PA 12. It could be explained by increment of soft rubber phase in the system. Furthermore, it is also seen that the TPVs show lower tension set and tan δ values than that of pure PA 12. This means the TPVs have higher elasticity or higher capability to recover to initial form after applying external force. It is interesting to highlight that the MDNRG/PA 12 TPVs exhibits lower tension set values compared with the DNRG/PA 12 TPVs counterpart. This is clear that the chemical interaction between the phases, is responsible to provide higher elasticity to the blend.

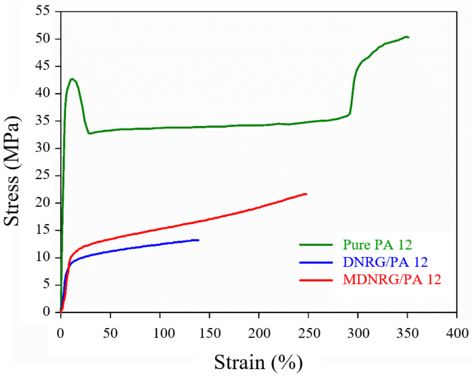

Figure 2. Stress-strain behaviors of pure PA 12, DNRG/PA 12 TPVs and MDNRG/PA 12 TPVs.

3.3 Confirmation of chemical interaction between MDNRG and PA 12 phases by ATR-FTIR

Figure 3 shows the ATR-FTIR spectra of pure PA 12 and its blends with DNRG and MDNRG. To confirm the presence of chemical interaction, unreacted PA 12 phases were previously separated by solvent extraction (i.e., dimethyl sulfoxide) prior to examine through the ATR-FTIR technique [17]. In Figure 3, it is seen that the pure PA 12 shows the characteristic peaks at the wavenumbers of 3297, 1633 and 1556 cm^{-1} which assign to –NH stretching, –C–O stretching and –NH bending vibrations, respectively. Furthermore, the absorption peaks of functional groups in PA 12 molecules at 3297, 1633 and 1556 cm^{-1} are also observed in the infrared spectra of the MDNRG/PA 12 TPVs despite extraction of PA 12 phase, however they are not observed in the spectrum of DNRG/PA 12 TPVs. It is interesting that some PA 12 molecules could not be extracted from the MDNRG/PA 12 TPVs due to strong chemical interaction between the phases, which is illustrated in Figure 4. That is, the interaction between the succinic anhydride groups in the form of cyclic or opened ring and polar functional groups of PA 12. These mechanisms are through (1) the covalent bonding between succinic anhydride and amide group and (2) hydrogen bonding arise from succinic anhydride and carbonyl group available in PA 12 structure.

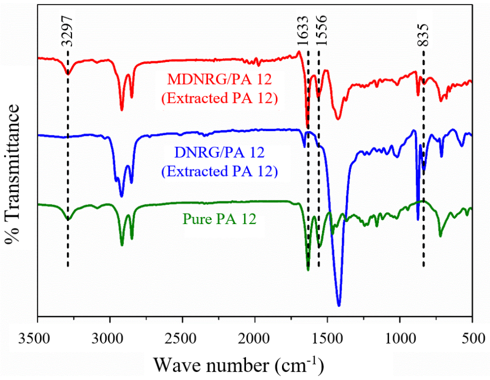

Figure 3. Infrared spectra for pure PA 12, DNRG/PA 12 TPVs and MDNRG/PA 12 TPVs.

Table 3. Mechanical properties, hardness and dynamic properties of devulcanized rubber/PA 12 TPVs with different types of DNRGs.

Properties	**Samples**		
	Pure PA 12	**DNRG/PA 12**	**MDNRG/PA 12**
Modulus at 100%	33.7 ± 0.1	12.4 ± 0.2	15.3 ± 0.1
Tensile strength (MPa)	50.3 ± 0.3	13.2 ± 0.4	21.6 ± 0.1
Elongation at break (%)	351 ± 22	139 ± 28	248 ± 19
Hardness (Shore A)	94.0 ± 0.3	92.3 ± 0.3	90.8 ± 0.3
Tension set (%)	84.0 ± 1.4	54.5 ± 1.4	44.8 ±1.2
tan δ	0.98	0.42	0.39

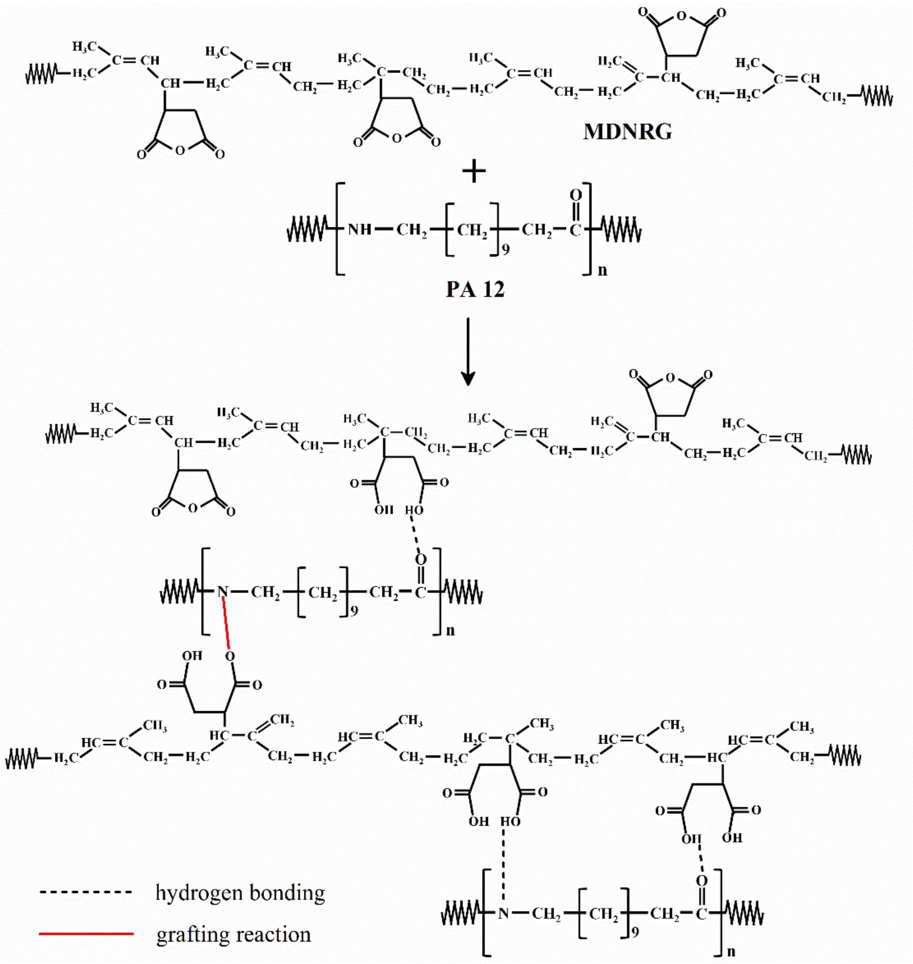

Figure 4. Possible reaction mechanism between MDNRG and PA 12 molecules at the interface.

3.4 Temperature scanning stress relaxation characterization

The temperature scanning stress relaxation or TSSR can be used to characterize thermomechanical behavior of rubber-like materials such as, vulcanized rubber or thermoplastic elastomer material [18, 19]. Normalized force versus temperature curves of both TPVs is shown in Figure 5. It is obviously seen that the MDNRG/PA 12 TPVs provided higher normalized force versus temperature curve than that of the DNRG/PA 12 TPVs. This reflects better in thermo-elastic behavior or the superior relaxation behavior of MDNRG/PA 12 TPVs than the DNRG/PA 12 TPVs. This is attributed to the chemical interaction between polar functional groups in PA 12 molecules and succinic anhydride groups of MDNRG molecules which was mentioned previously and also illustrated in Figure 4. As data summarized in Table 4, it is clear that the MDNRG/PA 12 TPVs provided higher force at starting temperature (F_0), rubber index (RI), and T_{10} T_{50} and T_{90} values. This indicates that the MDNRG/PA 12 TPVs has higher elastomeric behavior which related to the RI value and thermal resistance as observed from higher values of T_{10}, T_{50} and T_{90}.

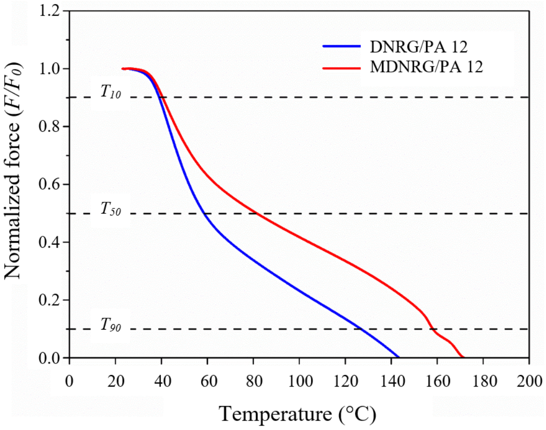

Figure 5. Normalized force-temperature curves of devulcanized rubber/PA 12 TPVs with different types of DNRGs.

Table 4. TSSR Results of devulcanized rubber/PA 12 TPVs with different types of DNRGs

Properties	**Samples**	
	DNRG/PA 12	**MDNRG/PA 12**
F_0 (MPa)	4.45	7.09
T_{10} (°C)	39.1	40.6
T_{50} (°C)	58.6	81.5
T_{90} (°C)	126.8	158.1
Rubber index (RI)	0.47	0.51

3.5 Morphological properties

SEM micrographs of the solvent-etched cryogenic fractured surfaces of both TPVs are shown in Figure 6. In this work, the PA 12 phase was preferential extracted by dissolving in hot dimethyl sulfoxide (DMSO) and hence the vulcanized rubber domains were left adhering at the surfaces. It can be seen that all blends display two phases system in which dispersion of vulcanized rubber domains in the PA 12 matrix are observed. Additionally, it is clearly seen that the vulcanized rubber domains of MDNRG/PA 12 TPVs represented smaller particles size when compared to the vulcanized rubber domains of DNRG/PA 12 TPVs. That is, the average particle size of vulcanized rubber domains, in the MDNRG/PA 12 TPVs, is about 0.24 µm (Figure 6(b)). On the other hand, the DNRG/PA 12 TPVs had a larger average size of vulcanized rubber domains, namely about 0.68 µm (Figure 6(a)). These might be attributed to chemical interaction at the interfaces, as described and proved in Figures 3, 4 and 5. This is in good agreement to mechanical strength (Table 3), rubber elasticity in terms of the highest slope of the normalized force-temperature curve of the TSSR measurement (Figure 5), tension set and Tan δ (Table 3) observed in the preceding session.

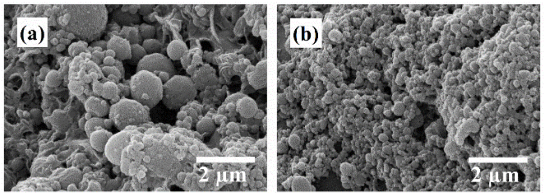

Figure 6. SEM micrographs of extracted devulcanized rubber/PA 12 TPVs with different types of DNRGs: (a) DNRG and (b) MDNRG with a magnification 7,000X.

4. Conclusions

Modification of DNRG molecules with maleic anhydride was successfully prepared. FTIR technique was used to confirm the presence of various functional groups on MDNRG backbone. It was found that rubber elasticity of PA 12 is relatively increased after blending with devulcanized rubber proving the formation of novel PA 12 material with good damping properties. Moreover, the MDNRG/PA 12 TPVs exhibited greater mechanical properties and rubber elasticity compared to the DNRG/PA 12 TPVs. This is attributed to chemical interaction between polar functional groups in the PA 12 molecules and anhydride groups in the MDNRG molecules which have been proved by ATR-FTIR and TSSR techniques. This result shows good agreement with higher area underneath of the normalized force-temperature curves and thermal resistance based on TSSR measurement. Moreover, SEM images show that the MDNRG/PA 12 TPVs have smaller micron-sized vulcanized rubber domains dispersed in the PA 12 matrix than that of the DNRG/PA 12 TPVs.

5. Acknowledgements

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References

[1] K. Chatterjee and K. Naskar, "Development of thermoplastic elastomers based on maleated ethylene propylene rubber (m-EPM) and polypropylene (PP) by dynamic vulcanization," *Express Polymer Letters,* vol. 1, pp. 527-534, 2007.

[2] M. R. Abadchi, A. J. Arani, and H. Nazockdast, "Partial replacement of NR by GTR in thermoplastic elastomer based on LLDPE/NR through using reactive blending: Its effects on morphology, rheological, and mechanical properties," *Journal of Applied Polymer Science,* vol. 115, pp. 2416-2422, 2010.

[3] L. Meszaros, M. Fejos, and T. Barany, "Mechanical properties of recycled LDPE/ EVA/ground tyre rubber blends: Effects of EVA content and post irradiation," *Journal of Applied Polymer Science,* vol. 125, pp. 512-519, 2012.

[4] M. M. Hassan, N. A. Badway, M. Y. Elnaggar, and E. A. Hegazy, "Synergistic effect of gamma radiation and peroxide on dynamic vulcanization of thermoplastic vulcanizes based on (de-vulcanized rubber)/polypropylene," *Journal of Vinyl and Additive Technology,* vol. 20, pp. 168-176, 2014.

[5] B. Sripornsawat, A. Kaesaman, and C. Nakason, "Thermoplastic Natural Rubber of Co-Polyamide: Effect of Blend Ratios on Mechanical, Swelling, Dynamic and Morphological Properties," *Advanced Materials Research,* vol. 844, pp. 89-92, 2014.

[6] H. Heping, L. Sidong, and P. Zheng, "Preparation and study of epoxidized natural rubber," *Journal of Thermal Analysis and Calorimetry,* vol. 58, pp. 293-299, 1999.

[7] M. Subhra, P. G. Mukundab, and G. B. Nando, "Thermal analysis of blends of poly(ethylene-co-acrylic acid) (PEA) and epoxidised natural rubber (ENR)," *Polymer Degradation and Stability,* vol. 50, pp. 21-28, 1995.

[8] C. Nakason, A. Kaesaman, and P. Supasanthitikul, "The grafting of maleic anhydride onto natural rubber," *Polymer Testing,* vol. 23, pp. 35-41, 2004.

[9] C. Nakason, S. Saiwari, and A. Kaesaman, "Rheological, thermal and morphological properties of maleated natural rubber and its reactive blending with poly(methyl methacrylate)," *Polymer Testing,* vol. 25, pp. 656-667, 2006.

[10] N. Hinchirana, W. Lertweerasirikun, W. Poonsawad, G. L. Rampel, and P. Prasassarakich, "Hydrogenated natural rubber blends: aspect on thermal stability and oxidative behavior," *Journal of Applied Polymer Science,* vol. 113, pp. 1566-1575, 2009.

[11] W. Arayapranee, and G. L. Rempel, "Morphology and mechanical properties of natural rubber and styrene-grafted natural rubber latex compounds," *Journal of Applied Polymer Science,* vol. 109, pp. 1395-1402, 2008.

[12] S. Salaeh, T. Banda, V. Pongdong, S. Wießner, A. Das, and A. Thitithammawong, "Compatibilization of poly(vinylidene fluoride)/natural rubber blend by poly(methyl methacrylate) modified natural rubber," *European Polymer Journal,* vol. 107, pp. 132-142, 2018.

[13] P. Intharapat, D. Derouet, and C. Nakason, "Thermal and flame resistance properties of natural rubber-g-poly(dimethyl(methacryloyloxy-methyl)phosphonate)," *Journal of Applied Polymer Science,* vol. 115, pp. 255-262, 2010.

[14] B. Sripornsawat, C. Nakason, and A. Keasaman, "Effect of modified natural rubber on properties of thermoplastic natural rubber based on Co-polyamide blends," *Advanced Materials Research,* vol. 626, pp. 233-236, 2013.

[15] S. Pichaiyut, C. Nakason, C. Kummerlowe, and N. Vennemann, "Thermoplastic elastomers based on epoxidized natural rubber/ thermoplastic polyurethane blends: influence of blending technique," *Polymers for Advanced Technologies,* vol. 23, pp. 1011-1019, 2012.

[16] H. M. Li, H. B. Chena, Z. G. Shenb, and S. Linb, "Preparation and characterization of maleic anhydride-functionalized syndiotactic polystyrene," *Polymer,* vol. 43, pp. 5455-5461, 2002.

[17] M. Narathichat, C. Kummerlowe, N. Vennemann, and C. Nakason, "Thermoplastic natural rubber based on polyamide-12: influence of blending technique and type of rubber on temperature scanning stress relaxation and other related properties," *Journal of Applied Polymer Science,* vol. 121, pp. 805-814, 2011.

[18] N. Vennemann, K. Bokamp, and D. Broker, "Crosslink density of peroxide cured TPV," *Macromolecular Symposia,* vol. 245, pp. 641-650, 2006.

[19] A. Barbe, K. Bokamp, C. Kummerlowe, H. Sollmann, and N. Vennemann, "Investigation of modified SEBS-based thermoplastic elastomers by temperature scanning stress relaxation measurements," *Polymer Engineering & Science,* vol. 45, pp. 1498-1507, 2005.