

ภาคผนวก

เอกสารตีพิมพ์ในการประชุม (proceeding) จากการเผยแพร่ผลงานวิทยานิพนธ์ในงานประชุม

International Polymer Conference of Thailand (PCT-6)

ณ Pathumwan Princess Hotel กรุงเทพมหานคร

ระหว่างวันที่ 30 มิถุนายน – 1 กรกฎาคม 2559

Improved Properties of Natural Rubber/Reclaimed Rubber/Propylene Ethylene Copolymer Thermoplastic Vulcanizates as Affected by Modifying Methods

Witchuda Nakasan, Sitisaiyidah Saiwari and Anoma Thitithammawong*

Department of Rubber Technology and Polymer Science, Faculty of Science and Technology,

Prince of Songkla University, Pattani Campus, Pattani, 94001, Thailand

Phone +66 73 312213, *E-Mail: anoma.t@psu.ac.th

Abstract

Thermoplastic vulcanizates (TPVs) based on natural rubber, reclaimed rubber and propylene ethylene copolymer NR/RR/PEC blends at blend proportion of 30/30/40 wt% were prepared. The effect of modifying methods on mechanical, rheological and morphological properties of TPVs was studied. It was found that TPV with phenolic resin showed better tensile strength, elongation at break and tendency to recover from prolonged extension than the TPV without modifier. Moreover, rheological properties and phase morphology were also improved with the addition of phenolic. The melt blending method gave the TPV with better overall properties than those of the reactive blended TPV. Further increase phenolic content the better phase compatibility was achieved.

Keywords: Thermoplastic vulcanizates, Natural rubber, Reclaimed rubber, Modifying methods, Phenolic resin

1. Introduction

Increasing high consumption of rubber products leads to large amount of rubber wastes disposed to environment. More than million tons of rubber wastes, mainly used tires, are still be the environmental problems [1] as their molecules are crosslinked and they need very long time for completely natural degradation.

Reclamation is one technique using either thermal mechanical or chemicals to recycle the waste of crosslinked rubbers [2]. After reclamation, reclaimed rubber can be partially vulcanized again and it is partly used as raw rubber in new rubber product for cost reduction. However, reclaimed rubber in general has poor mechanical properties in comparison to virgin rubbers. Also, it has inferior physical and/or chemical compatibility with other rubbers or polymers leading to phase separation of developed rubber compound [3]. Therefore, phase compatibility is a significant issue for use of reclaimed rubber in order to achieve vulcanizates with acceptable properties [4]. Many research works have been done on study the way to improve compatibility between reclaimed rubber and other polymers. For example, surface modifications of RR have been done to

improve the compatibility of RR with a polymer matrix [5-7]. Maleic anhydride (MA), bitumen, and allylamine were preferably applied as modifying agent to promote blend compatibility by increasing of phase adhesion [5-9]. Various irradiation techniques and plasma treatment were also used to activate reactive sites in the blends containing reclaimed rubber [10-11]. The reactive sites chemically reacted among phase and increased phase compatibility.

Propylene ethylene copolymer (PEC) offers an outstanding combination of clarity, heat-sealability, elasticity, softness, processability, and compatibility in blends in film, sheet, and molded products. It has been used as thermoplastic phase for production of TPVs with regard to good impact strength and processability [12-13].

In the present work, TPVs based on NR/RR/PEC blends were prepared at a blend ratio of NR/RR/PEC = 30/30/40 wt% by dynamic vulcanization. Effect of modifying methods and phenolic resin contents on the properties of the blends were investigated.

2. Experimental

2.1 Materials

Ribbed smoke sheet no.3 typed natural rubber (NR) was produced by Local Farmer Cooperation, Pattani, Thailand. Reclaimed rubber (RR) was purchased from Union Commercial Development Co., Ltd. Samutprakan, Thailand. Propylene ethylene copolymer, versify®3300, (PEC) was supplied by Dow Chemical Company, USA. Hydroxymethylol phenolic resin (HRJ-10518) manufactured by Schenectady International Inc, USA was used as modifying agent. Stannous chloride dehydrate (SnCl₂·2H₂O) used as a catalyst for phenolic resin was manufactured by Carlo Erba Reagent (France). The compound ingredients were zinc oxide (Global Chemical, Thailand), stearic acid (Imperial Chemical, Thailand), white oil (Maoming Fulida Chemical, China), wingstay L (Eliokem, USA), *N*-tert-butyl-2-benzothiazyl sulfenamide or TBBS (Flexys, USA), and sulfur (Siam Chemical, Thailand). All ingredients were used as received.

2.2 Preparation of NR/RR/PEC blends

NR/RR/PEC blends were prepared at a fixed blend ratio of 30/30/40 wt% in an internal mixer using compound formulation as given in Table 1.

Table 1. Compound formulation of NR/RR/PEC TPVs.

Ingredients	Quantity (phr)
NR	100
RR	90
PEC	67
HRJ-10518	0, 3, 5, 7, 10
SnCl ₂ ·2H ₂ O	1
Aromatic oil	10
Stearic acid	1
ZnO	5
Wingstay L	1
TBBS	0.8
Sulphur	4

* RR, containing 55.5% rubber content

** Blend ratio of NR/RR/PEC at 30/30/40 wt%

Mixing conditions were set at a fill factor of 0.80, mixing temperature of 155°C and at a rotor speed 60 rpm. In the present work, phenolic modifier was incorporated into the prepared blends in two different mixing methods. They were melt mixing and reactive blending as schematic diagram illustrated in Fig. 1. The blend without addition of modifier (called control) was also done for a comparison purpose. After completion of mixing, the mixture was removed from the chamber, immediately sheeted out on two roll mills and kept at room temperature for one day before further process. Test specimens were later prepared by compression molding at 165°C and preconditioned before test and characterization. In addition, the procedure which give the best properties of NR/RR/PEC TPV was later chosen and use in the part of study the effect of modifier content.

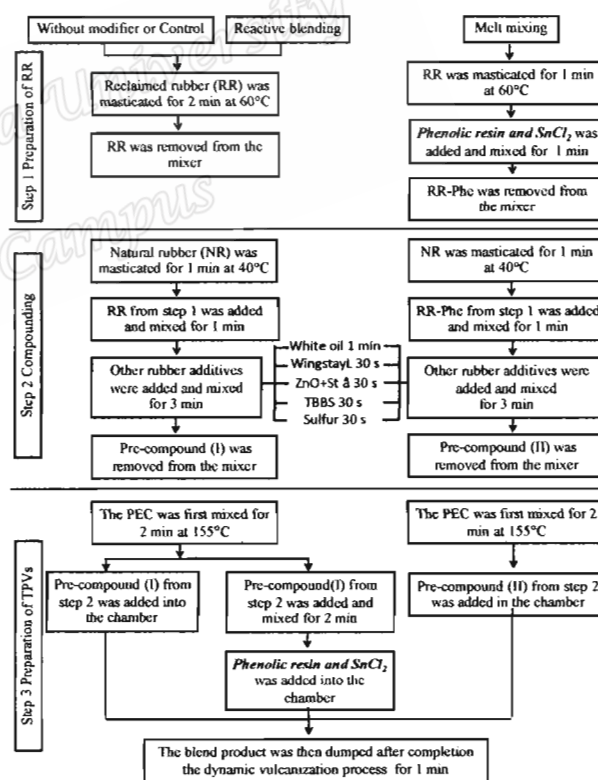


Fig. 1 Schematic diagram for mixing procedure for the preparation of NR/RR/PEC TPVs.

2.3 Testing procedures

2.3.1 Mechanical Properties

Tensile properties were measured on dumbbell shape

specimens using a Hounsfield Tensometer H 10 KS (the Hounsfield Test Equipment Co., Ltd, U.K.) in accordance with the procedure described in ASTM D412 at a constant cross-head speed of 500 mm/min. Tension set was tested at room temperature after stretching the samples for 10 min at 100% strain. Three specimens were tested for each sample and average value was reported.

2.3.2 Dynamic properties

Dynamic properties of the TPVs were established using a rotorless oscillating shear rheometer (RheoTech MDPT, Cuyahoya Falls, USA) at 165°C. The oscillation frequency was set in the range of 1–10 Hz at a constant strain of 3%. This was to ensure that the test was located in the linear viscoelastic region.

2.3.3 Morphological properties

Scanning electron microscope (model VP 1450, Leo, UK) was employed to examine morphology of extracted surface of NR/RR/PEC TPVs. The samples were cryogenically fractured in liquid nitrogen. The PEC phase was preferentially extracted by immersing the fractured surface into toluene for 30 minutes. The samples were dried in an oven at 40°C for 24 h to eliminate the solvent, and gold coated before characterization.

3. Results and Discussion

3.1 Effect of modifying methods on properties of NR/RR/PEC TPVs

Fig. 2 shows stress-strain curves of the NR/RR/PEC TPVs. It is seen that all TPVs show similar values of the initial slope at the beginning of the curves. All stress-strain curves of the TPVs behaved the character of soft and tough elastic material. Slight increase of modulus and tensile stress can be seen in the TPVs with addition of modifier. The NR/RR/PEC TPV with melt mixing method show highest tensile strength with more or less the same value of elongation at break when compared with the reactive blended TPV and the TPV without modifier. Furthermore, improvement of phase compatibility in the presence of modifier can be clearly seen from decreased tension set of the TPVs with modifier as shown in Fig. 3. This can be explained by a function of phenolic resin. That is, during melt blending,

graft copolymer of rubbers with phenolic resin occurred due to reactive methanol groups in the phenolic molecules can easily react with double bonds in the rubber chains [14] as reaction scheme shown in Schemes 1. This graft copolymer later reacted with rubber and PEC phases to form chemical reaction among phase [14]. Hence, increase of higher stress for tensile deformation and failure and also improvement of tension set are seen in Fig. 2 and 3.

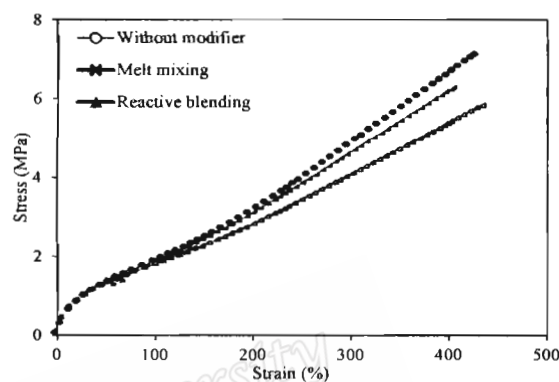


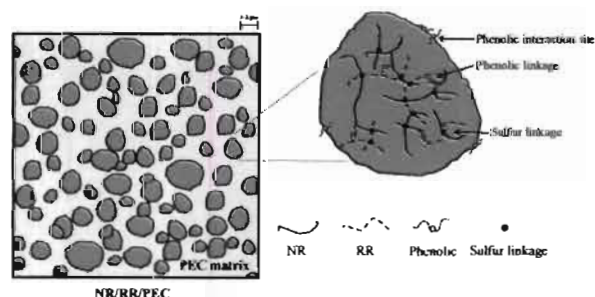
Fig. 2 Stress-strain curve of NR/RR/PEC TPVs prepared by different modifying methods.



Fig. 3 Tension set of NR/RR/PEC TPVs prepared by different modifying methods.

In addition, comparing between two modifying methods used, the melt mixing NR/RR/PEC TPV which phenolic resin was located in the RR phase seemed to give better tensile strength and elongation at break than the reactive blending TPV. This is attributed to in the melt mixing process graft copolymer of RR with phenolic (RR-Phe) was firstly prepared. This graft copolymer can further compatible with the NR phase. Therefore, the interfacial adhesion of rubber component in the investigated blend system is promoted leading to more

compatible rubber phase prior to mix with the PEC [15-17]. Moreover, addition of phenolic resin at the beginning of mixing process, there was an enough mixing time for phenolic to possess chemical reaction when compared to the reactive blending method. In the reactive blending, phenolic resin was added in the step 3 with short time for dispersion and reaction in the blend component. Therefore, this might be a reason that the NR/RR/PP TPV with reactive blending had inferior mechanical properties in relative to those of the melt mixing TPV.



Scheme 1. Possible reaction between phenolic resin and natural rubber.

Dynamic mechanical properties of NR/RR/PEC TPVs with variation of modifying methods were also studied and results are shown in Fig. 4. Results show material characteristic of pseudoplastic or shear thinning behavior. In addition, storage modulus and complex shear viscosity (Fig. 4(a) and (b)) slightly increased with incorporation of phenolic resin. Also, $\tan \delta$ clearly decreased to lower value (Fig. 4(c)). These observations are due to the phenolic modifier caused improvement of interfacial interaction among phases. The occurrence of chemical reaction by means of phenolic resin resulted in higher shear torque for molecular movement to desired strain [18]. As a consequence, storage modulus and complex shear viscosity of NR/RR/PEC TPVs with modifier were higher than those of the control TPV at a given tested frequency. In the case of $\tan \delta$, a drop of $\tan \delta$ means material has good elastic response with low damping in its molecules. The chemical reaction promoted by phenolic resin helped polymer molecules of the modified NR/RR/PEC TPVs can better relax applied

stress with low heat generated in molecules or loss modulus leading to low value of $\tan \delta$.

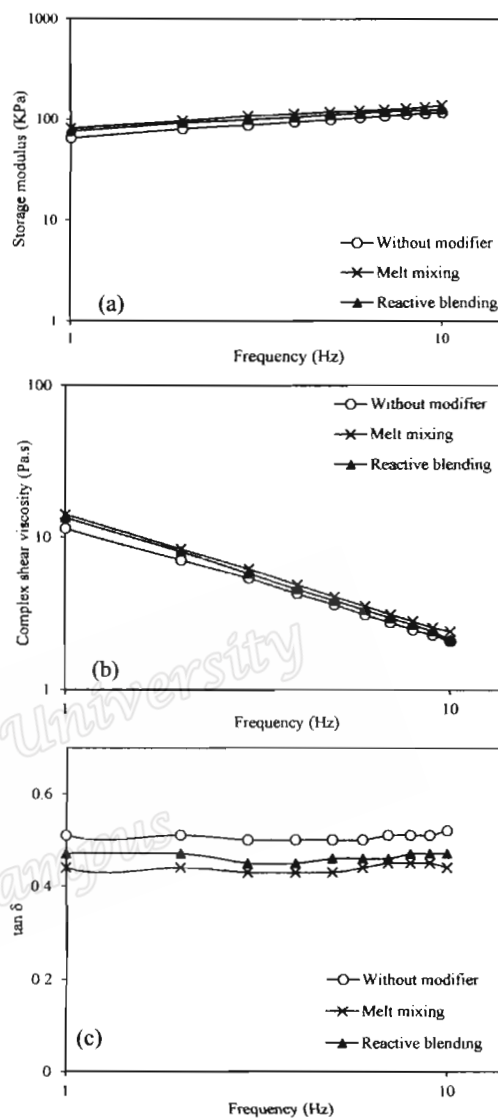


Fig. 4 Dynamic properties in a term of (a) storage modulus, (b) complex viscosity and (c) $\tan \delta$ as function of frequency of NR/RR/PEC TPVs with various modifying methods.

Focusing on two different modifying methods, the TPVs prepared by melt mixing and reactive blending had identical test results of storage modulus and complex shear viscosity. However, the melt mixing technique gave the TPV with lowest $\tan \delta$. This is because of different incorporation step of phenolic resin as discussed earlier. The melt mixing method allowed the phenolic to firstly locate in the RR phase before further reacted with NR and

PEC. In combination, this method provided enough time for phenolic to disperse and function. Therefore, the melt mixing showed stronger effect on phase compatibility of the TPVs.

Morphological study of the NR/RR/PEC TPVs was investigated using secondary electron SEM mode. Fig. 5 shows SEM micrographs of the toluene extracted surface of the NR/RR/PEC TPVs with various modifying methods. It is seen that the blends with different modifying method exhibited different surface morphologies. The surface morphology of the TPV without modifier (the control) and the TPV prepared by reactive blending method were more roughness than the surface morphology of the TPV prepared by melt mixing. The more roughness fracture surface means that the interfacial adhesion of the blend component is poor [9]. Incorporation of phenolic resin by means of melt mixing provides more smooth surface of the TPV than the others as an affected of chemical reaction caused by phenolic resin [19].

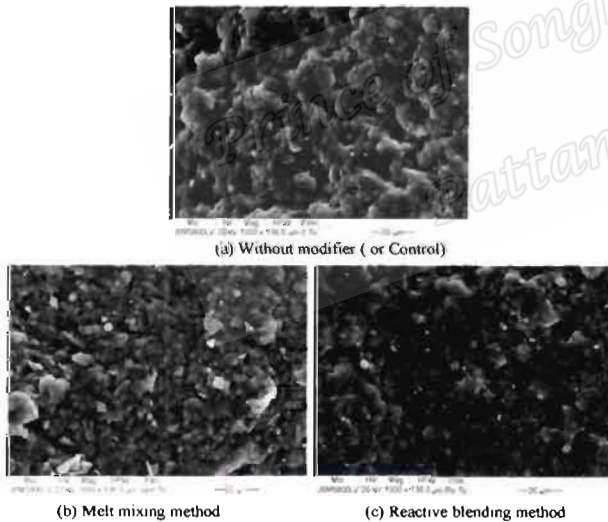


Fig. 5 SEM micrographs of NR/RR/PEC TPVs prepared by various modifying methods.

3.2 Effect of quantity of phenolic resin on properties of NR/RR/PEC TPVs prepared by melt mixing method

From previous study, the melt mixing process was chosen and used in the study of influence of quantity of phenolic resin. Figs. 6 and 7 show mechanical properties of the NR/RR/PEC TPVs. It is seen that tensile strength increased with increasing quantity of phenolic resin from

0 to 10 phr while as elongation at break and tension set slightly decreased. This was due to the raising of phenolic resin can perform more chemical interaction between RR and NR resulting to more compatible rubber phase which later dispersed in the PEC matrix with good interfacial adhesion. Additionally, small drop of tension set at 5 phr of phenolic resin might be attributed to an excess amount of phenolic resin caused phase separation and slightly hardened the TPV.

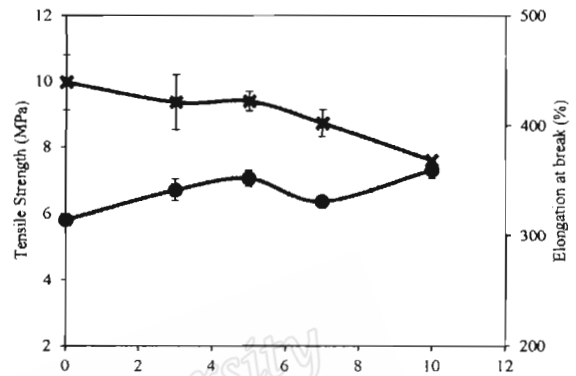


Fig. 6 Effect of phenolic resin content on the tensile strength and elongation at break of NR/RR/PEC TPVs.

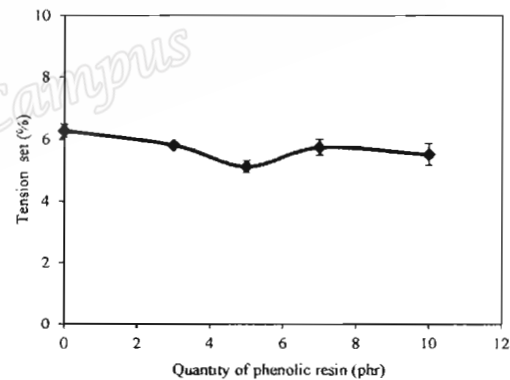


Fig. 7 Effect of phenolic resin content on tension set of NR/RR/PEC TPVs.

Fig.8 shows dynamic mechanical properties of the NR/RR/PEC TPVs with varying quantity of phenolic resin. Higher compatibility in the TPV can be seen from gradual increasing of storage modulus and complex shear viscosity together with decreasing of tan δ. At very high test temperature i.e. 165°C, the TPV almost melted as thermoplastic having vulcanized rubber particles as filler. The molten TPV was flowed in a direction of force (shear torque). Higher interfacial adhesion among phases yielded higher shear force for molten TPV to flow. Therefore,

increasing of storage modulus and complex shear viscosity were observed with increasing the phenolic content. Furthermore, good phase compatibility caused better stress relaxation at the interface and hence lower damping in polymer molecules as clearly noticed from the lower $\tan \delta$.

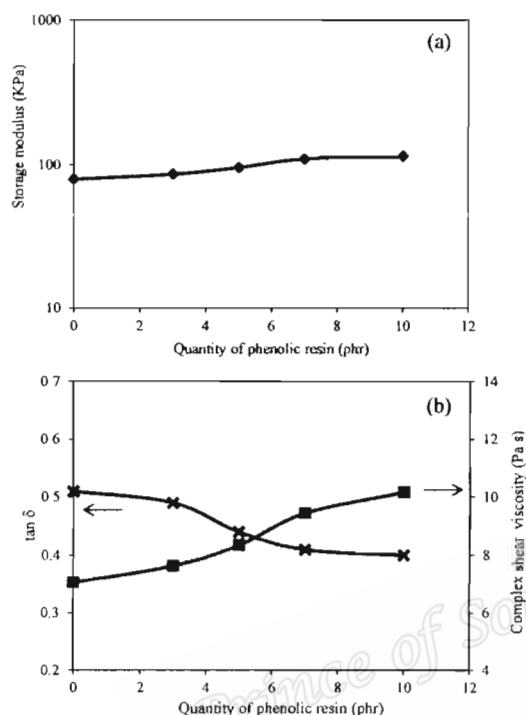
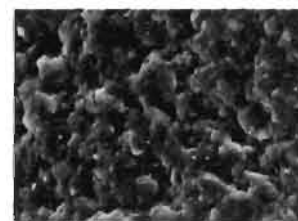


Fig. 8 (a) Storage modulus and (b) complex viscosity and $\tan \delta$ at a frequency of 2 Hz of NR/RR/PEC TPVs with phenolic resin content.

Fig. 9 shows SEM micrographs of the NR/RR/PEC TPVs with varying phenolic content. Finer phase morphology of the fractured surface TPVS was obviously seen with increasing content of phenolic resin. This morphology is corresponding to the results of mechanical and dynamic properties of the NR/RR/PEC TPVs. Increasing of interfacial adhesion among phases as previously discussed yielded to an improvement of phase compatibility. Therefore, finer phase distribution or smooth fractured surface of the TPVs with increasing the phenolic content was found. This developed morphology impacted on improvement of mechanical, dynamic, and rheological properties of the TPVs in previously results.

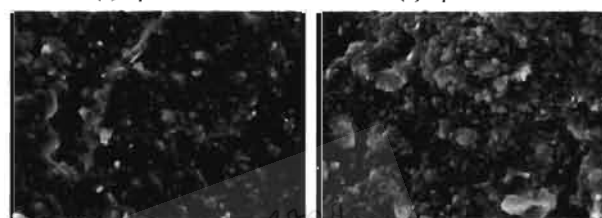


(a) 0 phr



(a) 3 phr

(a) 5 phr



(a) 7 phr

(a) 10 phr

Fig. 9 SEM micrographs of NR/RR/PEC TPVs with phenolic content.

4. Conclusion

The properties of NR/RR/PEC TPVs are affected by modifying method. The presence of phenolic modifier could promote improvement of mechanical, dynamic, and rheological properties of the modified NR/RR/PEC TPVs. The melt mixing method was the best method used for addition of phenolic resin due to this method provided enough time for chemical reaction of phenolic with other polymers phases and also it controlled the location of the phenolic in the RR phase. Quantity of phenolic content impacted on properties of the TPVs as well. It was seen that property improvement of TPVs can be clearly seen with increasing phenolic content in the blend system.

References

- [1] Duangburong, J., Tantayanon, S., Bhandhubanyong, P. "A breakthrough challenge with tyre waste management: thailand perspective", *Int. J. Soc. Sci. Human.*, 5, 768-772 (2015).
- [2] Isayev, A.I., "Recycling of rubbers", In: Erman, B., Mark, J.E., Roland, C.M. (eds) *The science and*

- technology of rubber, United states of America: 697-764 (2013).
- [3] Ramarad, S., Khalid, M., Ratnam, C.T., Chuah, A.L., Rashmi, W. "Waste tire rubber in polymer blends: A review on the evolution, properties and future", *Prog. Mater. Sci.*, 72, 100-140 (2015).
- [4] Fan, P., Lu, C. "A study on functionalization of waste tire rubber powder through ozonization", *J. Polym. Environ.*, 19, 943-949 (2011).
- [5] Shanmugaraj, A.M., Kim, J.K., Ryu, S.H. "Modification of rubber powder with peroxide and properties of polypropylene/rubber composites", *J. Appl. Polym. Sci.*, 104, 2237-2243 (2007):
- [6] Naskar, A.K., De, S.K., Bhowmick, A.K. "Thermoplastic elastomeric composition based on maleic anhydride-grafted ground rubber tire", *J. Appl. Polym. Sci.*, 84, 370-378 (2002).
- [7] Zhang, S.L., Xin, Z.X., Zhang, Z.X., Kim, J.K. "Characterization of the properties of thermoplastic elastomers containing waste rubber tire powder", *Waste Manage.*, 29, 1480-1485 (2009).
- [8] Lu, X., Wang, W., Yu, L. "Waste ground rubber tire powder/thermoplastic vulcanizate blends: Preparation, characterization, and compatibility", *J. Appl. Polym. Sci.*, 131, 39868 (2014).
- [9] Lee, S.H., Balasubramanian, M., Kim, J.K. "Dynamic reaction inside co-rotating twin screw extruder. II. Waste ground rubber tire powder/polypropylene blends", *J. Appl. Polym. Sci.*, 106, 3209-3219 (2007).
- [10] Hassan, M.M., Badway, N.A., Elnaggar, M.Y., Hegazy, E.S.A. "Thermo-mechanical properties of devulcanized rubber/high crystalline polypropylene blends modified by ionizing radiation", *J. Ind. Eng. Chem.*, 19, 1241-1250 (2013).
- [11] Zhang, X., Zhu, X., Liang, M., Lu, C. "Improvement of the properties of ground tire rubber (GTR)-filled nitrile rubber vulcanizates through plasma surface modification of GTR powder", *J. Appl. Polym. Sci.*, 114, 1118-1125 (2009).
- [12] Rajeshbabu, R., Gohs, U., Naskar, K., Thakur, V., Wagenknecht, U., Heinrich, G. "Preparation of polypropylene (PP)/ethylene octene copolymer (EOC) thermoplastic vulcanizates (TPVS) by high energy electron reactive processing", *Radiat. Phys. Chem.*, 80, 1398-1405 (2011).
- [13] Da Silva, A.L.N., Rocha, M.C.G., Coutinho, F.M.B., Bretas, R., Scuracchio, C. "Rheological, mechanical, thermal, and morphological properties of polypropylene/ethylene-octene copolymer blends", *J. Appl. Polym. Sci.*, 75, 692-704 (2000).
- [14] Nakason, C., Nuansomsri, K., Kaesaman, A., Kiatkamjornwong, S. "Dynamic vulcanization of natural rubber/high-density polyethylene blends: Effect of compatibilization, blend ratio and curing system", *Polym. Test.*, 25, 782-796 (2006).
- [15] Jose, S., Thomas, S., Parameswaranpillai, J., Aprem, A.S. Kocsis, J. "Dynamic mechanical properties of immiscible polymer systems with and without compatibilizer", *Polym Test.*, 44, 168-176 (2015).
- [16] Ohlsson, B., Hassander, H., Törnell, B. "Effect of the mixing procedure on the morphology and properties of compatibilized polypropylene/polyamide blends", *Polymer*, 39, 4715-4721 (1998).
- [17] Thipmanee, R., Lukubira, S., Ogale, A.A., Sane, A. "Enhancing distributive mixing of immiscible polyethylene/thermoplastic starch blend through zeolite ZSM-5 compounding sequence". *Carbohydr. Polym.*, 136, 812-819 (2016).
- [18] Nakason, C., Saiwari, S., Kaesaman, A. "Rheological properties of maleated natural rubber/polypropylene blends with phenolic modified polypropylene and polypropylene-g-maleic anhydride compatibilizers", *Polym. Test.*, 25, 413-423 (2016).
- [19] Pichaiyut, S., Nakason, C., Kaesaman, A., Kiatkamjornwong, S. "Influences of blend compatibilizers on dynamic, mechanical, and morphological properties of dynamically cured maleated natural rubber and high-density polyethylene blends", *Polym. Test.*, 27, 566-580 (2008).