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The use of reclaimed rubber from waste tires for production of dynamically cured natural rubber/reclaimed rubber/polypropylene blends: effect of reclaimed rubber loading

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Abstract

Reclaimed rubber (RR) from waste tires was introduced into thermoplastic vulcanizates (TPVs) based on blends of natural rubber (NR)/RR/polypropylene (PP). The curing characteristics of NR/RR compounds together with properties of TPVs, i.e., mixing and dynamic vulcanization behaviors and mechanical, dynamic and morphological properties, were investigated with respect to RR content. The results show that the RR affects static and dynamic vulcanization of rubber molecules by increasing cure rate but lowers curing efficiency. Increasing the RR content in NR/RR/PP TPVs slightly reduces tensile strength but with a sharp impact on elongation at break. Dynamic properties reveal that elastomeric response of NR/RR/PP TPVs is inferior relative to that of NR/PP TPV. However, the complex viscosity indicates improved processability of the TPVs. SEM micrographs confirm dispersed phase morphology with vulcanized NR and RR particles embedded in the PP matrix, and the particle size increases with RR content.

1. Introduction

The growing use of automobiles generates a large volume of used tires that are discarded creating an extremely challenging waste problem. Unlike thermosplastics, vulcanized rubber waste cannot be recycled and reprocessed, as the rubber molecules are chemically crosslinked. Incineration and landfill are the basic methods to solve the problem, but they can cause severe environmental problems such as air pollution and contamination of environment by leaching of toxic components [1-3]. Reclamation and devulcanization are nowadays claimed to be effective methods for the reuse of vulcanized rubber waste, and under proper processing conditions the rubber molecules can be re-crosslinked [1,4,5]. These processes require either biological (microorganism) [6,7], physical [8-10], thermal-mechanical [11,12], chemical [13-15], or mechano-chemical [16] treatments cutting the rubber networks at main chains and/or at crosslink bridges. Efficiency of reclamation and devulcanization depends on the process and conditions used, and is quantified by sol fraction, degree of rubber swelling, crosslink density, molecular weight, and molecular weight distribution [11, 17].

To simplify complicated rubber processing, thermosplastic vulcanizates (TPVs) have been developed. TPVs are new class of materials prepared by melt blending an elastomer with a crystalline thermoplastic, and dynamically vulcanizing the elastomers phase [18]. TPVs possess elastomeric properties at service temperature, have a low temperature utilization, and can be processed and shaped using thermoplastic processing equipment, which is simpler than the production of conventional rubber products [18,19]. Furthermore, the unique morphology with crosslinked rubber particles embedded in the hard matrix leads to superior mechanical properties of the TPVs. Natural rubber/polypropylene (NR/PP) TPVs have been developed and studied by many researchers [20-23]. This polymer pair shows good compatibility due to inherent match of the molecular structures, and possesses outstanding elastomeric properties, i.e., low damping and permanent set and good elongation at break [23-24].

A potential utilization of reclaimed rubber from waste tires in production of TPVs has been studied. Main objectives are improvement of TPV's mechanical and thermal properties and cost reduction. There are many reports on the use of recycling rubber as main elastomer part in TPV by blending with many types of crystalline thermoplastics for example polyethylene [25-26], polypropylene [8,9,27], polyamide [28-29], poly(butylene terephthalate) (PBT) [30]. Another option is addition of reclaimed rubber as a third component in TPV [31-33]. However, this method is complicated due to the blend system needs to be balance between phase dispersion and distribution and phase compatibilization in order to boot TPV properties.

In the present work, reclaimed rubber (RR) from waste tires was added into the compound formulation of NR at various contents. The effect of RR on curing characteristics of NR compounds was investigated.

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Then NR/RR/PP TPVs were later prepared. The influences of RR on mixing behavior, mechanical properties, and dynamic rheological and morphological properties of the NR/RR/PP TPVs were measured and are discussed.

2. Experimental

2.1 Materials

The natural rubber (NR) used was a standard Thai natural rubber (STR 5L), purchased from Yala Latex Co., Ltd., Thailand. Reclaimed rubber (RR) from waste tires having density of 0.95 g/cm^3 was supplied by the Union Commercial Development Co., LTd., Thailand. The main components of the RR are 57% rubbers and 35% fillers. It has a sol fraction of 49%. SEM micrograph of the obtained commercial RR is shown in Figure 1. Polypropylene homopolymer (PP, Moplen HP500N) with a melt flow rate of 12 g/10 min (measured at 230^{o}C/2.16 kg) and a density of 0.90 g/cm^3 was supplied by HMC Polymers Co., Ltd., Thailand. White oil was supplied by Conocophillips Co., Ltd., USA. Zinc oxide (ZnO, Zinkoxydaktiv®) was manufactured by Lanxess Deutschland GmbH, Germany. Stearic acid activator (Palmac 1500) was manufactured by Imperial Chemical Co., Ltd., Pathum Thani, Thailand. Sulfur used as a curing agent was manufactured by Utids Enterprise Co., Ltd., Samut Sakhon, Thailand. N-tert-butyl-2-benzothiazyl sulfonamide (TBBS) and N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6-PPD) were pruduced by Flexsys, Belgium. All the materials were used as received without further purification.

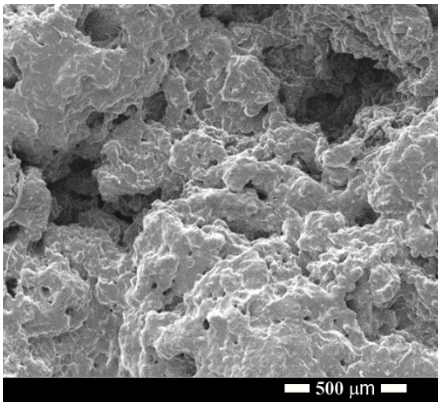

Figure 1. Microscope image of raw reclaimed rubber.

2.2 Preparation of rubber compounds and TPVs

Rubber compounds were firstly prepared by mixing NR, RR and rubber additives in an internal mixer (Brabender Plasticorder model PLE331, Brabender OHG Duisburg, Germany) at 40^{o}C under a rotor speed of 60 rpm with 85% fill factor. The compounding formulations and mixing steps of compounding are shown in Table 1. The total mixing time of each batch was 10 min, and the compounds were then sheeted out on a two-roll mill and left at room temperature for at least 24 h prior to fabricating and testing curing characteristics. The NR/RR/PP TPVs were later prepared by melt blending the PP (40 parts) with the NR/RR compound (60 parts). The mixing was done at 170^{o}C for 5 min in an internal mixer with a rotor speed of 60 rpm and 85% fill factor. The mixing torque-time curve was recorded. The TPV product was then passed through the two-roll mill to form a sheet before compression molding at 180^{o}C to create the test specimens. In this work, the RR quantity was varied (0, 15, 30, 45, or 60 phr) in the rubber compound and the properties of NR/RR/PP TPVs were investigated.

Table 1. Compound formulation, mixing time and mixing steps for rubber blends.

Mixing time (min)	Chemicals	Quantity (phr)
0	NR	100
1	RR	0, 15, 30, 45, 60
2	White oil	10.0
3	-	-
4	ZnO	5.0
5	Stearic acid	2.0
6	6PPD	1.0
7	TBBS	1.5
8	Sulfur	2.5
9	-	-
10	Compounding finished in 10 min	

2.3 Testing and characterization

Curing characteristics Cure characteristics of the NR compounds were determined using a moving die rheometer (MDR; Rheoline Mini MDR Lite, Prescott Instruments Ltd, Gloucestershire, UK) according to ASTM D5289 at 1.67 Hz frequency and at 180°C.

Tensile properties A universal tensile testing machine (Hounsfield Tensometer, model H 10KS, Hounsfield Test Equipment Co., Ltd, Surrey, U.K.) was used to determine the tensile properties of TPVs in accordance with ASTM D412. Test specimens were shaped with die cut type C. The test was done at room temperature, with an extension speed of 500 mm/min. Tensile strength and elongation at break were then reported. Tension set was also measured by using the tensile testing machine. The test started by applying force to dumbbell shaped specimen until the extension reached 200%. The sample was then stretched for 10 min under applied force before taking out and allowing the sample to retract in a specific manner for another 10 min. Tension set was later calculated using equation 1.

$$Tension\ set\ (\%) = \frac{L - L_0}{L_0} \times 100 \qquad (1)$$

where L is the length remaining between gage marks after testing (cm) and L_0 is the original length between gage marks before testing (cm).

Dynamic properties Dynamic behavior of the TPVs was measured with a moving die processibility tester (RheoTech MDPT, Cuyahoya Falls, USA) at 180°C. The oscillation frequency sweeps were performed over the range 0.01-100 rad/s at a constant strain amplitude of 3%, which was in the linear viscoelastic range. The storage (G') and loss (G'') shear moduli, tan δ, as well as complex viscosity (η^*) of the TPVs were recorded.

Morphological study Morphologies of the TPVs were characterized using FEI Quanta-400 (FEI Company, USA) scanning electron microscope (SEM). The TPV samples were fractured in liquid nitrogen, the PP phase was removed by extraction with hot xylene, the samples were dried in an oven and were then sputter coated with gold prior to SEM imaging.

3. Results and Discussion

3.1 Curing characteristics of NR/RR compounds

Curing curves of the NR/RR compounds with various RR contents are shown in Figure 2. It is seen that the compounds had curing reversion with increasing curing time. Increasing the RR content in the compound decreased the cure rate and efficiency. Decaying slope of the curing curves (from minimum to maximum torque) implies that the curing rate was delayed by the RR. Curing efficiency of the NR/RR compounds is also quantified by scorch time (T_{s1}), cure time (T_{90}) and torque difference (M_H-M_L), shown in Figure 3. The slight decrease of scorch time and cure time, together with the sharp drop of M_H-M_L, reveal that molecular crosslinks were formed faster but reached lower crosslink density as RR content was increased. These observations are attributed to the fact that the RR molecules are shorter than the raw NR molecules due to scission during reclamation. Also, there are active crosslink sites present in the RR molecules for re-crosslinking [12,17]. Small molecules and active sites need comparatively low activation energy for the reaction, so that decreased scorch and cure times were observed with RR addition, as seen in Figure 3. Furthermore, the observed decreases in curing slope and torque difference are due to dilution effects. The RR and fillers (43% of carbon black and $CaCO_3$ in RR, proved by TGA) diluted the crosslink agent in the rubber compound.

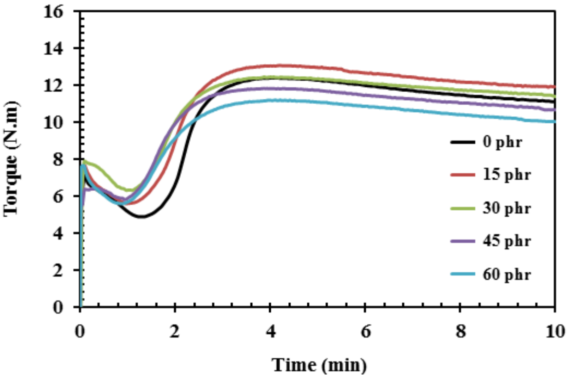

Figure 2. Curing behavior of NR/RR compounds at various RR loadings.

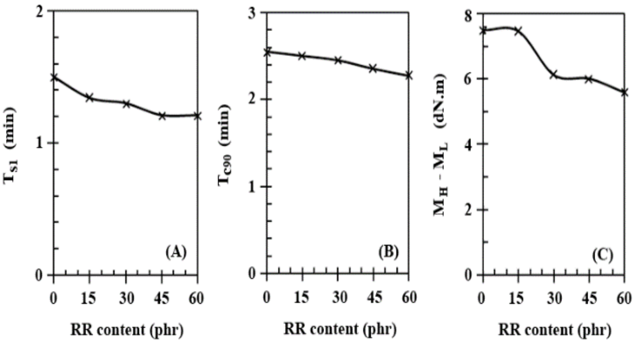

Figure 3. Scorch time, cure time and torque difference of NR/RR compounds at various RR loadings.

3.2 Mixing torque and dynamic vulcanization behavior

The NR/RR/PP TPVs were prepared by dynamic vulcanization in an internal mixer and the mixing torque-time curves were recorded. Figure 4 shows the mixing torque-time curves of TPVs. It is noted that the mixing torques show similar patterns, except in the period of dynamic vulcanization. The addition of RR at various loadings into the NR/RR compound affects dynamic vulcanization behavior of the rubber phase in the TPVs. The mixing torques at different mixing positions, seen in Figure 5, were observed and are summarized in Figure 6. It is seen that the dynamic vulcanization behaviors of the TPVs are similar to the curing characteristics shown in Figures 2 and 3. The initial time of dynamic vulcanization, time of completed dynamic vulcanization, and torque differences of dynamic vulcanization decreased with RR content. This is due to the short molecular chains with highly active crosslink sites in the RR molecules, as described previously. However, in the curves of Figure 6 an inflection point with RR loading is clearly observed at 15 phr. RR contents beyond the inflection point cause obvious changes in the dynamic vulcanization behavior of TPV, while up to that point it is almost constant (at RR loadings of 30-60 phr). This is because the mixing had dynamic flow of a molten blend under high shear. The crosslink reactions and chain scissions were rapid. Therefore, the influence of very high loadings of RR in the TPVs is not clear, unlike in the static curing test by MDR.

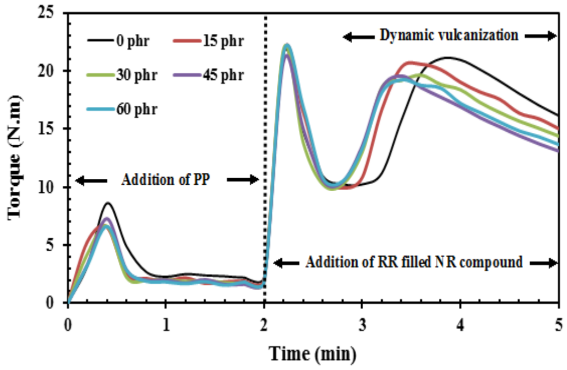

Figure 4. Mixing torque of NR/RR/PP TPVs at various RR loadings.

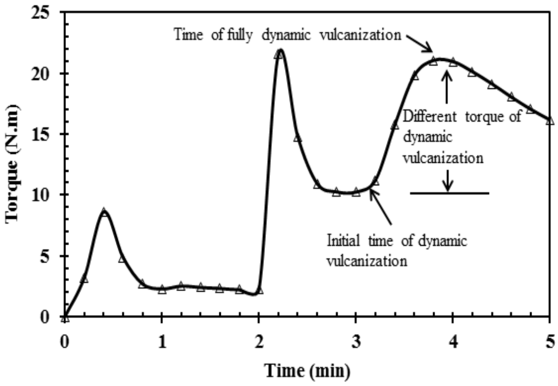

Figure 5. Time trace of the mixing torque of 60/0/40 NR/RR/PP TPVs.

3.3 Tensile properties

Stress-strain curves of the NR/RR/PP TPVs are shown in Figure 7. The plots show that the TPVs are toughness material which high stiffness. The increase of RR content does not impact on Young's modulus but it has significant effect on tensile modulus and strength of TPVs. It is seen that tensile modulus tends to decrease with the RR content. Values of tensile strength and elongation at break of the NR/RR/PP TPVs are then summarized in Figure 8. The results show that tensile strength changes slightly while the elongation at break clearly decreases with RR content in the TPV. This means that the TPV loses toughness. The observations can be explained by the crosslink density of rubbers and also by the presence of fillers in RR component of the TPV. At the fixed 60/40 blend ratio by weight of rubbers/PP, the decrease of crosslinking and the increase in filler loading are so balanced that they cause little change in tensile strength with RR loading changes. However, they have a large effect on the elongation at break. The different vulcanization rates of NR and RR together with the low curing efficiency give the TPVs inferior resistance to stretching. Furthermore, filler in the RR phase can restrict the molecular mobility in this phase.

Tension set of TPVs was also measured with the results shown in Figure 9. The permanent deformation of TPVs improved with RR content. This contrasts the consistent loss of elongation at break. The explanation might involve the three-dimensional network structure of reclaimed rubber [12,34], which lowers tension set when RR elastomer particles are dispersed in the crystalline PP matrix.

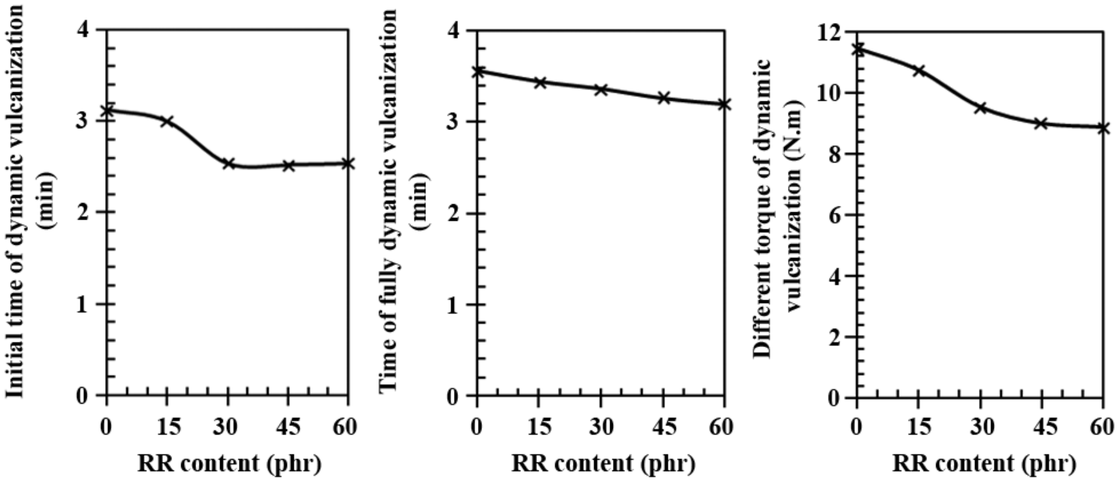

Figure 6. Initial time of dynamic vulcanization (A), time of completed dynamic vulcanization (B), and torque difference in dynamic vulcanization (C) of the NR/RR/PP TPVs at various RR loadings.

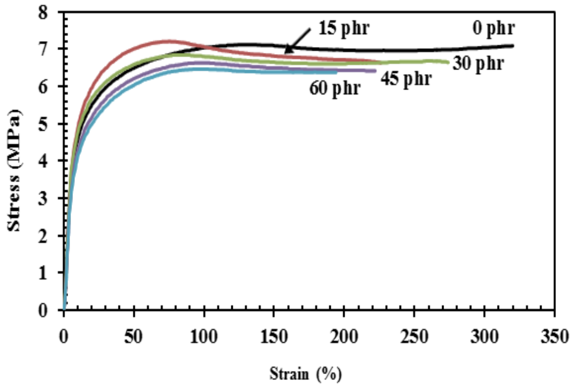

Figure 7. Stress-strain curves of the NR/RR/PP TPVs at various RR loadings.

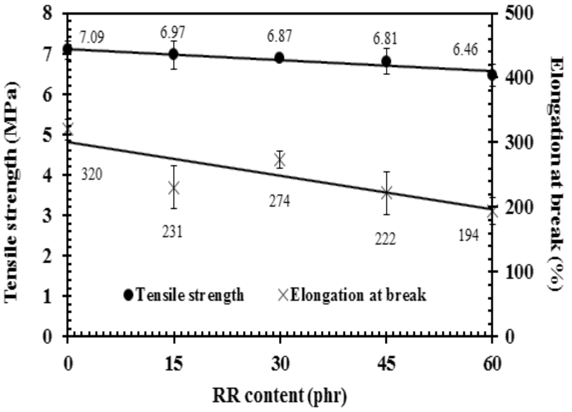

Figure 8. Tensile strength and elongation at break of the NR/RR/PP TPVs at various RR loadings.

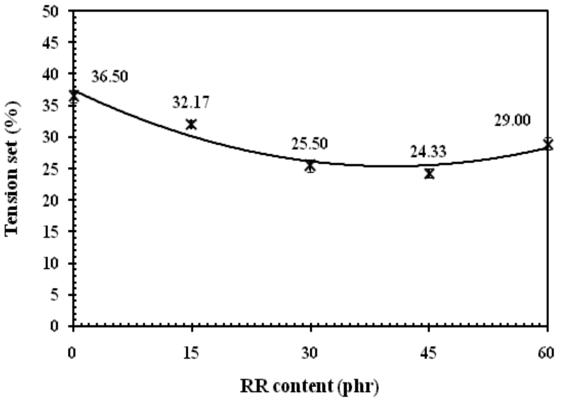

Figure 9. Tension set of the NR/RR/PP TPVs at various RR loadings.

3.4 Dynamic properties

Dynamic properties of the TPVs measured by MDPT are given in Table 2. It is noted that both storage modulus (G') and tan δ of TPVs first declined with the addition of RR at 15 phr before increasing with further addition. The loss modulus (G") continually increased. In macroscopic observations, the small RR molecules dispersed in the TPV system soften the material modulus by decreasing G' from that of the NR/PP TPV. However, the higher G" and tan δ of all the NR/RR/PP TPVs reveals that the dynamic-elastomeric response of TPVs with RR was poor. This is attributed to the synergistic effects of RR molecular weight, crosslink density, and fillers in the RR component. Complex viscosity (η*) of the TPVs was also measured and is presented in Table 2. The results reveal that the addition of RR into TPVs promotes processability, and this agrees with the results on G'.

Table 2. Dynamic properties of the NR/RR/PP TPVs.

RR contents (phr)	G' (kPa)	G" (kPa)	Tan δ	η* (Pa.s)
0	28.5	4.2	0.147	6,650
15	17.2	5.7	0.331	5,420
30	24.8	6.5	0.262	6,200
45	25.5	7.1	0.278	6,350
60	26.9	7.8	0.290	6,490

3.5 Morphological investigation

SEM micrographs of the prepared TPVs are shown in Figure 10. The micrographs show that the TPVs had dispersed phase morphology with the rubber particle size increasing with RR content. The NR/PP TPV (0 phr RR content) had the smallest vulcanized NR particles. This is due to the highest curing efficiency (see Figures 2 and 3) giving the NR phase much higher viscosity than the molten PP phase. Hence, the NR phase was broken up into small particles [23,24]. On the other hand, the addition of RR with short chains into the TPVs delays the curing reaction. This affects the viscosity difference of phases in the TPVs system. Therefore, the NR/RR/PP TPVs had comparatively larger vulcanized rubber particles. The morphology observations match well the results on tensile strength and elongation at break.

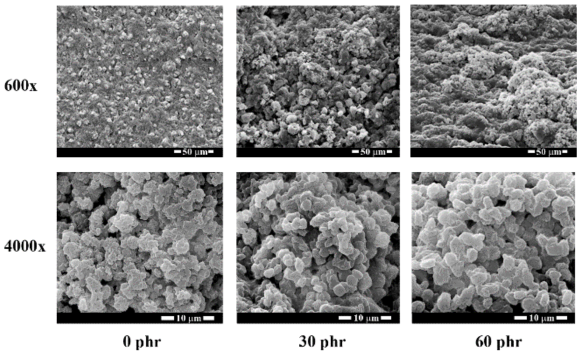

Figure 10. SEM micrographs of NR/RR/PP TPVs at various RR loadings.

4. Conclusions

The effects of various RR contents on the properties of NR/RR compounds and NR/RR/PP TPVs were investigated. Incorporation of RR speeded up curing but lowered curing efficiency, as seen in the curing characteristics of rubber compounds and in dynamic vulcanization of TPVs. Even small contents of RR caused loss of mechanical and dynamic properties of the NR/RR/PP TPVs from those of the neat TPV. The low molecular weight of RR molecules, crosslinking degree, and filler content in RR component of the TPV blend, contributed to the changes of properties. However, improved processability of TPVs was observed with RR content. SEM micrographs confirmed dispersed phase morphology of vulcanized NR and RR particles embedded in the PP matrix, and the size of dispersed particles increased with RR content.

5. Acknowledgements

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