

Polypropylene/Natural Rubber Thermoplastic Elastomer: Effect of Phenolic Resin as a Vulcanizing Agent on Mechanical Properties and Morphology

Varaporn Tanrattanakul,¹ Kesinee Kosonmetee,¹ Pasaree Laokijcharoen²

¹Polymer Science Program, Faculty of Science, Prince of Songkla University, Hadyai, Songkla 90112, Thailand

²National Metal and Materials Technology Center, Pathumthani 12120, Thailand

Received 4 August 2008; accepted 27 November 2008

DOI 10.1002/app.29816

Published online 3 March 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The aim of this study is to characterize thermoplastic elastomers (TPEs) from polypropylene and natural rubber with and without phenolic resin as a vulcanizing agent. The blends containing 40–60 wt % of polypropylene were mixed in an internal mixer and pressed with a compression molding machine. TPEs without rubber vulcanization, named as unvulcanized thermoplastic natural rubber (uTPNR) were compared to TPEs containing dynamic vulcanized rubber, referred as vulcanized thermoplastic natural rubber (vTPNR). The uTPNRs illustrated cocontinuous phase morphology, whereas the vTPNRs displayed dispersed phase of vulcanized natural rubber. Tensile properties, tear strength, thermal ageing resistance, ozone resistance, tension set, hardness and swelling test in toluene, IRM 903 oil and engine oil were carried out according to ASTM. It was found that tensile

and tear strength, hardness and tension set of the uTPNRs increased with increasing polypropylene content. Dynamic vulcanization improved tensile strength, elongation at break, tension set and degree of swelling of the TPEs, whereas hardness and tear strength did not show significant change after dynamic vulcanization. The vTPNRs exhibited higher ozone resistance and swelling resistance than the uTPNRs. Reprocessability of the vTPNRs was investigated and showed that tensile strength decreased at 20 and 30% and elongation at break decreased at 13 and 27% for the first and the third reprocessing respectively. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3267–3275, 2009

Key words: thermoplastics; vulcanization; blends; natural rubber; polypropylene

INTRODUCTION

Thermoplastic elastomers (TPEs) have been widely used in various applications. TPEs can be classified into two classes: block copolymers and polymer blends between plastic and rubber. TPEs synthesized from block copolymers includes thermoplastic styrene block copolymers and polyester TPEs.¹ Thermoplastic polyurethane (TPUs)¹ can be identified into this class although they are not block copolymer. TPEs prepared from polymer blends may be categorized into two types based on rubber vulcanization—thermoplastic olefins (TPOs) and thermoplastic vulcanizates (TPVs). TPOs often refer to the blends without rubber vulcanization and plastics normally

used are polyolefins, i.e., polyethylene and polypropylene. TPOs were introduced in the early 1970s, they were blends of EPDM and polyolefin plastic (usually PP) and rubber was slightly or not-at-all crosslinked.¹ Vulcanization in the rubber phase of TPVs has to occur during melt blending between plastic and rubber as called dynamic vulcanization. Dynamic vulcanization is attributed to phase inversion that is rubber morphology changes from cocontinuous phase to dispersed phase although rubber is the major component. This results in elastomeric characteristics in deformation properties at room temperature and thermoplastic manner in processing properties. Another advantage of TPEs is their recycling aspects. Relatively new class of elastomers is polyolefin elastomers (POEs). POEs are copolymers of ethylene and another α -olefin such as butane or octane as known in the name of ENGAGE (They are synthesized by using metallocene polymerization catalysts.

There were many articles reporting on TPEs prepared from polymer blends. The most widely used plastic is polypropylene (PP). Various rubbers were blended with PP to prepare TPEs such as ethylene–propylene–diene rubber (EPDM),² styrenic block

Correspondence to: V. Tanrattanakul (varaporn.t@psu.ac.th).

Contract grant sponsors: Prince of Songkla University, Graduate School, National Science and Technology Development Agency (Thailand Graduate Institute of Science and Technology Program); contract grant number: TGIST 01-49-045.

TABLE I
Formulation of Rubber Compounding

Chemical	Weight
NR	100
Stearic acid	2
Zinc oxide	5
Wingstay TM L	1
Phenolic resin	8

copolymer,^{2,3} ethylene propylene rubber (EPR),³ rubber waste from ground tread layers of truck tires⁴ and natural rubber.^{5–9} Natural rubber (NR) has been used to blend with polyethylene to prepare TPEs.^{10–12} Although PP/EPDM TPV is already commercialized, namely Santoprene (TPV prepared from PP and EPDM still has been extensively studied.^{13–24} Development in morphology and mechanical properties of PP/EPDM TPV were reported in many articles.^{13,15–17,19,20} Oil distribution between phases in this TPV was studied.^{18,21,24} Winter et al.¹⁴ used solid state ¹³C-NMR to determine the composition of TPVs. Effect of compatibilizer on mechanical properties and morphology of TPVs was reported by Nas-kar and Noordermeer²² and Thitithammawong et al.²³ Other rubbers used to prepare PP-based TPVs included epoxidized natural rubber,²⁵ acrylonitrile-butadiene rubber,^{26–28} ethylene-octene copolymer,²⁹ ethylene-methyl acrylate copolymer,³⁰ NR,^{31–35} and maleated NR.³⁶ TPV prepared from polyethylene blended with NR was also reported.^{37–41} Thermoplastic natural rubber (TPNR) was also named for the NR-based TPEs. Vulcanizing agents frequently used were sulfur, dicumyl peroxide and the mixture of both chemicals. Phenolic resin was used as the vulcanizing agent in TPV derived from the PP/EPDM blends^{14,17,19,21} and stannous chloride dehydrate was used together with phenolic resin to act as catalyst.^{14,19,21} Obviously, there are many attempts to prepare new TPVs from polymer blends because preparation of polymer blending is much easier than synthesis of a new polymer. NR is one of the well known conventional rubbers; low cost and abundant supply. Due to nonpolar characteristic, NR should be able to blend with PP but a compatibilizer might be needed because of the immiscibility nature of this blend. Although PP/NR blend have been studied; however, there are not many articles reporting on PP/NR TPE. The aims of this study were to prepare and characterize thermoplastic elastomer from PP and NR with and without phenolic resin (SP1045) as a vulcanizing agent. Both stannous chloride, used as an accelerator for phenolic resin, and a compatibilizer were not applied to the blends. Abbreviation of the blends with and without rubber vulcanization was vulcanized thermoplastic natural rubber

(vTPNR) and unvulcanized thermoplastic natural rubber (uTPNR) respectively. They were compared in terms of morphology and mechanical properties of the blends containing 40–60 wt % of polypropylene.

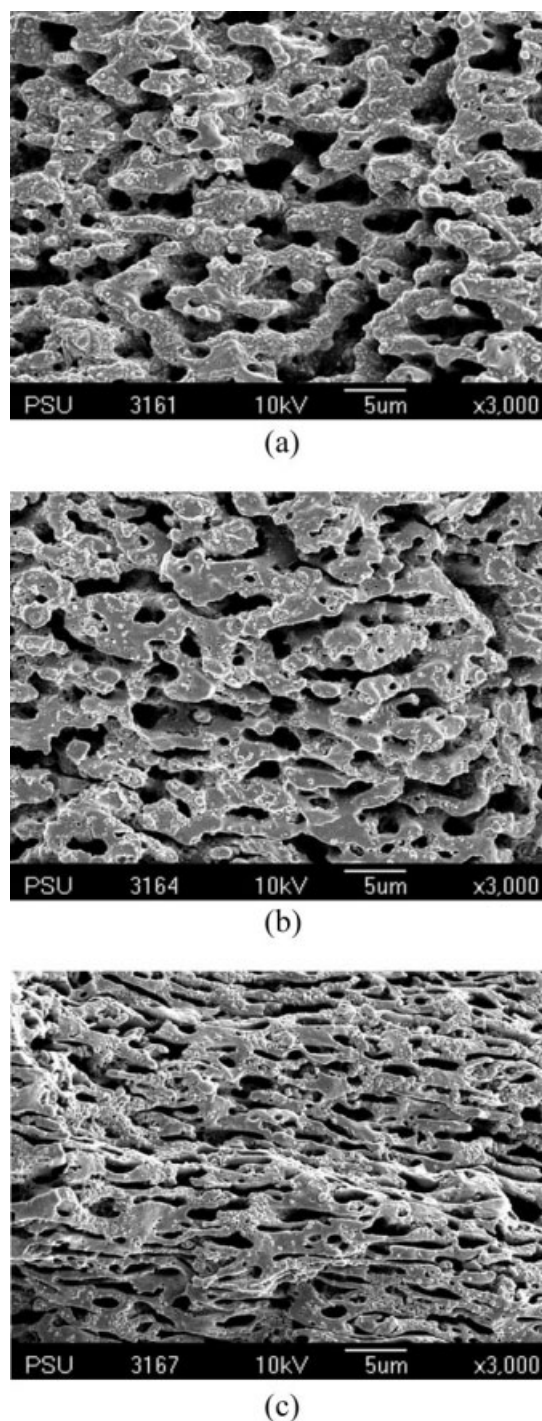


Figure 1 SEM micrographs of freeze fractured surface of uTPNRs after etching with benzene: (a) 40% PP, (b) 50% PP, and (c) 60% PP.

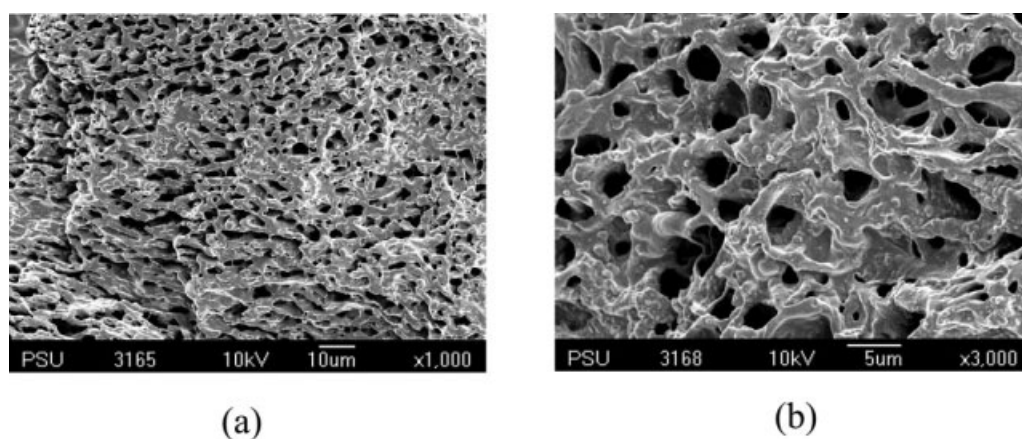


Figure 2 SEM micrographs of freeze fractured surface of uTPNRs after etching with *p*-xylene: (a) 50% PP, and (b) 60% PP.

EXPERIMENTAL

Materials

Polypropylene used was EL-Pro (P340J) produced by SCG Chemicals, Thailand. Melting temperature was 164°C and melt index was 1.8 g/10 min at 230°C under weight of 2160 g. Natural rubber, constant viscosity grade (STR5 CV60), was produced by Chana Latex Industry, Thailand. Phenolic resin (SP1045) was used as a vulcanizing agent and produced by Schenectady International. All chemicals for rubber compounding were commercial grade and used as received. Toluene (analytical grade, produced by Fisher Scientific), IRM 903 oil (equivalent to ASTM oil no. 3) and diesel engine oil (SAE 20W-50, produced by Mitsubishi Motors) were used in swelling test.

Thermoplastic elastomer preparation

Polymer blending was executed in an internal mixer [Brabender (Mixer 350E)], having a mixing chamber volume of 370 cm³, at 180°C and rotor speed of 60 rpm. NR was masticated with a two-roll mill before blending with PP. PP was allowed to melt for 3 min in the mixer before adding natural rubber. Two polymers were mixed in the mixer until the constant torque was obtained, which took ~ 5 min. For the blends without chemicals (uTPNRs), the blends were removed immediately from the mixer and passed through the two-roll mill once only to get a sheet. For preparing vTPNRs, chemicals were loaded in the last step and mixed continuously until the torque of mixing was constant. Then the blends were processed similarly to that of uTPNRs. Total mixing time was about 14 and 8 min for the blends with and without curing system respectively. After maturation time of 8 h, the sheets were pressed in a com-

pression molding machine [Kao Tieh (KT7014)] to obtain 2 mm thick sample at 170°C under pressure of 300 kg/cm² for 7 min. The sheets were then cooled down to room temperature under pressure of 150 kg/cm² for 5 min. The blend ratios between PP and NR were 40/60, 50/50, and 60/40 by weight. Formulation of rubber compounding was listed in Table I. The chemicals in Table I were based on natural rubber content. Vulcanization time of rubber compound was determined by using a moving die rheometer [Alpha Technology (MDR2000)] at 180 and 190°C. Rubber compound was prepared by using the internal mixer at 70°C with the rotor speed of 60 rpm before testing the optimum cure time (t_{90}) which represents to time at 90% of maximum torque during testing.

Mechanical properties and morphology investigation

Dumbbell-shaped tensile specimens and right-angle tear specimens were prepared for tensile properties and tear strength testing according to ASTM D412 Die C and ASTM D624 respectively, by using LLOYD LR10K under ambient environment with a testing speed of 50 and 500 mm/min at room temperature. Specimens (8–10) were tested for every sample. Thermal ageing resistance and hardness Shore A were investigated according to ASTM D573 and ASTM D2240 respectively. Ageing condition was 70°C for 7 days executed in a geer type forced ventilation oven [Tabai Espec (GPHH-100)]. The geer oven is equipped with a rotating rack for test specimens and is most suitable for the thermal ageing test of polymers. Changes in properties were calculated based on the difference between tensile properties after ageing and before ageing divided by the properties before ageing. Ozone resistance was determined in terms of changes in tensile properties

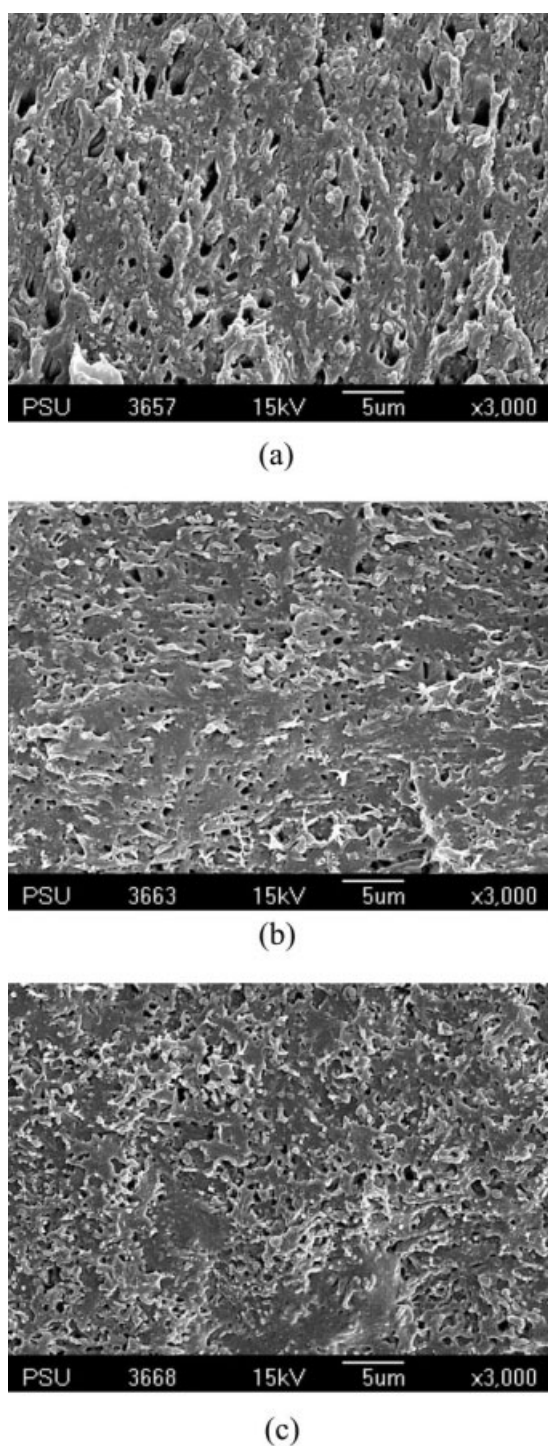


Figure 3 SEM micrographs of freeze fractured surface of vTPNRs after etching with benzene: (a) 40% PP, (b) 50% PP, and (c) 60% PP.

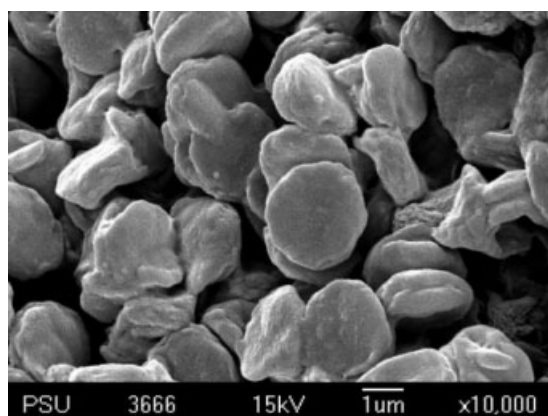
similarly to changes in thermal ageing resistance. Ozone measurement was carried out in a Toyoseiki EG2001 under an ozone concentration of 50 parts per hundred million (pphm) and a temperature of 40°C for 6 h. The testing specimens were extended for 20% elongation kept in a dark room for 48 h before applying ozone and kept at ambient environ-

ment after applying ozone for 12 h before tensile testing. Changes in tensile properties after ozone ageing were calculated similar to thermal ageing resistance. Tension set was carried out according to ASTM D412 method A and calculated based on the difference between a length after load releasing (L) and an original length divided by the original length. The crosshead speed was 40 mm/min. The 100% strain was maintained for 10 min L was measured after load releasing for 10 min. Six specimens were determined for each sample. Swelling test was operated at 30°C and reported as degree of swelling based on the difference between specimen weight after and before swelling divided by the weight before swelling. Three specimens were tested for every sample. Swelling time in toluene was 72 h, IRM 903 oil and engine oil was 168 h. Freeze fractured surfaces of the blends were photographed by a scanning electron microscope (SEM) [JEOL (JSM5800LV)]. The fractured surface was etched with benzene, a good solvent of NR, at 50°C for 24 h or with *p*-xylene, a good solvent of PP, at 110°C for 45 min to remove NR phase or PP phase on the fractured surface respectively. The specimens were vacuum dried at 70°C for 12 h before gold coating. To verify the reprocessing ability of the prepared thermoplastic vulcanizates (vTPNRs), the sample was reprocessed three times by compression molding. Initially four vTPNR sheets were prepared. The first sheet was tested for tensile properties. The second sheet was cut into $1 \times 1 \text{ cm}^2$ pieces and recompression molded under similar condition and tensile properties were investigated. For the third and fourth sheets, they went through twice and thrice the above process respectively.

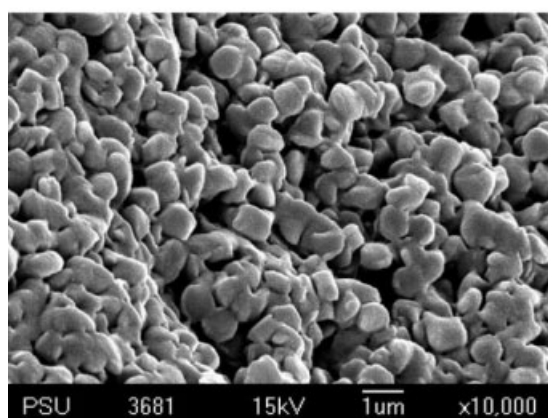
RESULTS AND DISCUSSION

Blend morphology

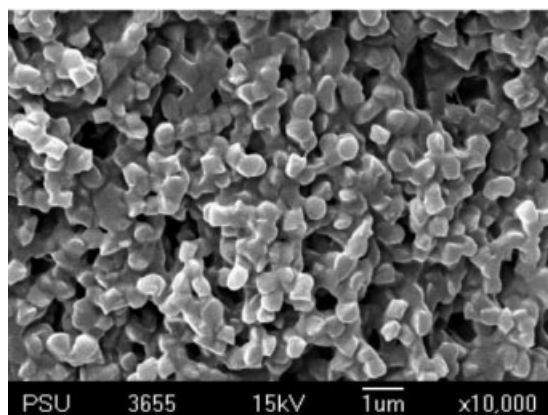
To investigate morphology of the blends, it is necessary to remove one phase before observation with the SEM. In the present study benzene and *p*-xylene were used for etching NR and PP from specimen surface respectively. Figure 1 showed SEM micrographs of uTPNRs after etching with benzene, whereby NR phase on the surface was removed. Continuous phase of PP was observed in all uTPNRs. Continuous phase of NR was seen in uTPNRs after etching with *p*-xylene that removed PP from the sample surface as shown in Figure 2. These results indicated that the prepared uTPNRs were cocontinuous phase. In contrast, the rubber phase in TPE prepared from PP/EPDM blend showed dispersed particles of EPDM^{13,20} attributed to better mechanical properties than the present uTPNRs.



(a)



(b)



(c)

Figure 4 SEM micrographs of freeze fractured surface of vTPNRs after etching with *p*-xylene: (a) 40% PP, (b) 50% PP, and (c) 60% PP.

The prepared vTPNRs exhibited continuous phase of PP and dispersed phase of NR as displayed in Figures 3 and 4 respectively. After etching with benzene, small holes were observed on the PP matrix (Fig. 3). These holes decreased in size with increasing PP content. The small particles of NR in vTPNRs shown in Figure 4 corresponded to the size of holes noticed in Figure 3. The vTPNRs containing 50 and

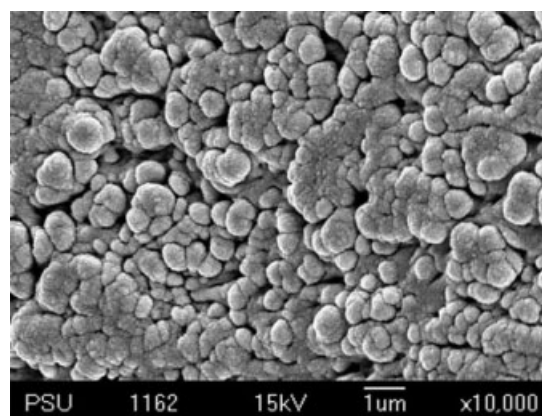


Figure 5 SEM micrographs of freeze fractured surface of *p*-xylene etched vTPNR containing 50% PP before compression molding.

60% PP showed submicron NR particles ($0.88 \pm 0.08 \mu\text{m}$ and $0.63 \pm 0.08 \mu\text{m}$ in diameter respectively) and the particle shape and size were similar to PP/PEDM TPV vulcanized with phenolic resin¹⁹ and vulcanized with peroxides,³⁵ while TPV containing 40% PP showed the NR particles with $2.13 \pm 0.20 \mu\text{m}$ diameter. This morphology, dispersed particles of NR, proved that dynamic vulcanization took place during melt blending in all blends. Evidence confirming the existence of the *in situ* vulcanization was the similar morphology obtained in the blend before compression molding as shown in Figure 5. Rubber particles diameter in 1–2 μm were generally reported for typical vTPNRs.³⁰ The PP/EPDM TPV may consist of rubber particles with 0.5–5 μm in diameter dispersed in PP matrix.²¹ The present NR particles were in the same range as general vTPNRs ($\leq 2 \mu\text{m}$). The change in morphology after dynamic vulcanization, from continuous phase to dispersed phase of NR as described above, caused changes in mechanical and physical properties as described below.

From various prior works dealing with making TPVs using SP1045 as the curing agent, it is not always mandatory to use stannous chloride as an

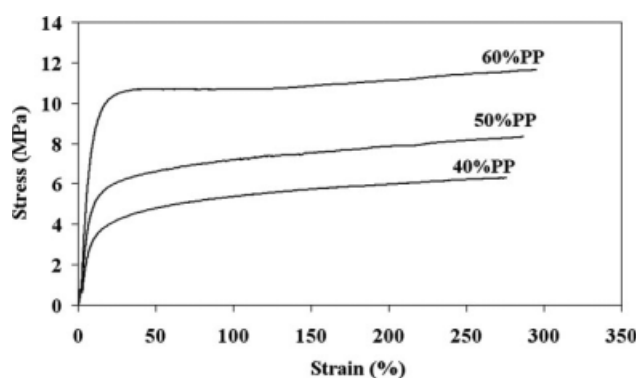


Figure 6 Stress-strain curves of uTPNRs containing 40–60% PP tested at 50 mm/min.

TABLE II
Tensile Properties of uTPNRs^a

PP (%)	Speed (mm/min)	E (MPa)	σ_y (MPa)	ε_y (%)	σ_b (MPa)	ε_b (%)
40	50	36.94 ± 8.09	3.26 ± 0.40	9.02 ± 1.47	5.34 ± 0.59	279 ± 25
	500	42.10 ± 7.33	3.35 ± 0.68	7.43 ± 0.58	4.94 ± 0.64	196 ± 38
50	50	69.26 ± 6.25	3.74 ± 0.34	10.07 ± 1.41	5.42 ± 0.63	282 ± 77
	500	79.93 ± 9.13	5.99 ± 0.34	7.57 ± 0.87	6.90 ± 1.18	211 ± 39
60	50	90.66 ± 5.69	9.30 ± 0.32	10.28 ± 0.47	10.94 ± 1.07	293 ± 76
	500	112.37 ± 9.20	8.08 ± 0.74	7.21 ± 0.13	9.58 ± 0.45	290 ± 84

^a Containing 40–60 wt % of PP tested at 50 and 500 mm/min.

accelerator. It is totally correct that the presence of stannous chloride in dynamic vulcanization process will happen faster; however, the faster curing is not at all times the main propose of the mixing, but a balance between the mixing rate and the curing rate should be achieve to obtain the best properties of TPVs. Furthermore, the rheometer test results showed that the t_{90} of NR compound was 14.12 and 9.17 min when tested at 180 and 190°C respectively. Therefore, in the present case the total mixing of 14 min at 180°C is enough to suffice the good dynamic vulcanization of this blend system.

Mechanical properties

Stress-strain curves and tensile properties of uTPNRs were demonstrated in Figure 6 and Table II respectively. The uTPNRs showed tensile behavior similar to ductile thermoplastics, i.e., polyolefins which showed unclear yield point and high ductility. The drawing strain was relatively constant compared with tensile behavior of vTPNRs as illustrated in Figure 7. Theoretically, yield stress is the stress at which material changes from elastic deformation to plastic deformation, causing it to deform permanently. It should be noted that yield point of polyolefins, e.g., polyethylene and polypropylene, is different from other ductile polymers, e.g., polycarbonate, poly(ethylene terephthalate) and polyamide. In the latter, yield coincides with the observation of a maximum stress in the stress-strain curve after elastic deformation. This is because after they have been loaded to their yield strength, necking as the cross-sectional area of the specimen decreases due to plastic flow occurred. The substantial necking causes a decrease in engineering stress as increasing engineering strain because of geometric effects—calculation assuming the original cross-sectional area. In contrast, polyethylene and polypropylene do not have a well-defined yield point because there is no such a neck taking place. One approach to determine yield stress on this stress-strain curve is where the

two tangents to the initial and final parts of the stress-strain curve intersect.⁴²

Generally, initial modulus changes significantly with testing speed, higher speed provides higher modulus. Tensile strength and elongation at break change slightly with testing speed. Yield strength and tensile strength of uTPNRs increased with increasing PP content, whereas elongation at break was still in the range of 200–290%. Tensile strength of the present uTPNRs was in the same range of PP/EPDM TPEs as reported by Cahkraborty et al.² It is common to observe the increase in tensile strength with increasing plastic phase due to the increase in rigidity of the blends. Dynamic vulcanization changed stress-strain behavior of the blends as shown in Figure 7. A decrease in yield stress and the appearance of strain hardening are remarkably noticed in Figure 7 whereas cold drawing without strain hardening was shown in Figure 6. Similar tensile behavior was observed in PP/EPDM TPV cross-linked with peroxide.¹⁶ Changes in morphology during stretching and yielding process in the TPV above were explained in details as well.¹⁶ The higher yield stress in uTPNRs may be due to the continuous phase of NR. In contrast, the change in morphology of NR from continuous phase to dispersed phase in vTPNRs caused a lower yield stress. Tensile

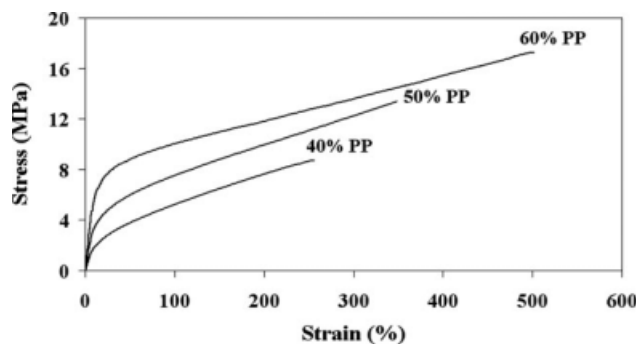


Figure 7 Stress-strain curves of vTPNRs containing 40–60% PP tested at 50 mm/min.

TABLE III
Tensile properties of vTPNRs^a

PP (%)	Speed (mm/min)	E (MPa)	σ_y (MPa)	ϵ_y (%)	σ_b (MPa)	ϵ_b (%)
40	50	18.82 ± 1.57	2.06 ± 0.13	10.97 ± 0.92	7.73 ± 0.74	255 ± 40
	500	31.79 ± 3.14	2.62 ± 0.33	8.26 ± 0.87	8.45 ± 1.16	229 ± 30
50	50	36.04 ± 2.40	3.81 ± 0.08	10.61 ± 0.92	14.64 ± 0.53	397 ± 31
	500	65.67 ± 13.34	4.66 ± 0.32	7.27 ± 1.30	15.47 ± 0.50	388 ± 37
60	50	59.06 ± 7.50	6.55 ± 0.43	11.24 ± 1.55	17.54 ± 0.51	506 ± 32
	500	114.39 ± 3.86	6.91 ± 0.63	6.66 ± 2.76	16.30 ± 0.83	439 ± 68

^a Containing 40–60 wt % of PP tested at 50 and 500 mm/min.

properties of vTPNRs were listed in Table III. Tensile strength and elongation at break increased, whereas modulus and yield stress decreased after dynamic vulcanization due to changes in NR morphology and the presence of crosslinks in NR. Without dynamic vulcanization, NR showed continuous phase resulting in high modulus and yield stress. After dynamic vulcanization, the dispersed particles of NR caused the reduction in modulus and yield stress of the blends. That is the continuous morphology restricts the flow or the movement of molecules. It is believed that tensile strength and elongation at break of TPV depend on dispersion morphology, the rubber domain size and distribution,¹⁷ and it is known that tensile strength and elongation at break of NR increased after vulcanization. As a result, the dynamic vulcanization increased tensile strength and elongation at break. Usually, in view of polymer blends there is an optimal particle size for each blend system and submicron particle size is mostly required. As shown in Figure 4, NR particle size decreased with increasing PP content; therefore, the vTPNRs containing 50 and 60% PP displayed much improved tensile strength and elongation at break than the vTPNR containing 40% PP. Compared to PP/MNR TPV,³⁶ the present vTPNRs showed somewhat higher tensile strength and much higher elongation at break for vTPNRs containing 50 and 60% PP.

Tear strength, hardness and tension set of uTPNRs were listed in Table IV. All properties increased with increasing PP content. Crosslinking affected

slightly tear strength and hardness of the blends as tabulated in Table V. Hardness of the present vTPNRs seemed to be lower than that of the PP/MNR vTPNRs.³⁶ Tension set of uTPNRs was very high, as high as 50%. This is due to the cocontinuous morphology of uTPNRs and flow ability of unvulcanized NR (thermoplastic nature). However, after dynamic vulcanization tension set of the blends decreased drastically (12–35%) and also decreased with increasing NR content (Table V). This is because of crosslinking in rubber phase.¹⁷ The lowest tension set obtained in the present study was 12% derived from the blend containing 40% PP. This value is lower than that of PP/ENR TPV containing 25% PP which were in the range of 15–20%.²⁵ Normally, more rubber concentration should provide lower tension set. It seems that morphology of NR in the present study and ENR in the report²⁵ seen to be different. The present NR particles were denser whereas those ENR particles showed cavitations. Unfortunately they did not report the size of the ENR particles.

In general, unvulcanized NR is a thermoplastic. The rubber elasticity of NR seems only after vulcanization in the appropriate concentration. As a result, it is not surprising to obtain high tension set in the PP/NR uTPNRs. Furthermore, it is difficult to compare this property with other uTPNRs containing EPDM and styrenic copolymers (SEBS). Because these elastomers are able to show rubber elasticity without vulcanization and the rubber phase could be dispersed as small particles resulting to good

TABLE IV
Tear Strength, Hardness and Tension Set of uTPNRs^a

PP (%)	Tear strength (N/mm)	Hardness (shore A)	Tension set (%)
40	62.79 ± 5.64	65.67 ± 2.31	43.75 ± 2.50
50	86.24 ± 3.37	83.33 ± 3.06	50.67 ± 4.04
60	109.23 ± 5.92	91.00 ± 1.00	56.67 ± 2.89

^a Containing 40–60 wt % of PP.

TABLE V
Tear Strength, Hardness and Tension Set of vTPNRs^a

PP (%)	Tear strength (N/mm)	Hardness (shore A)	Tension set (%)
40	58.15 ± 2.99	75 ± 3.46	12.00 ± 0.00
50	85.17 ± 2.46	87 ± 1.00	22.25 ± 2.06
60	108.56 ± 5.55	91 ± 0.00	35.00 ± 5.00

^a Containing 40–60 wt % of PP.

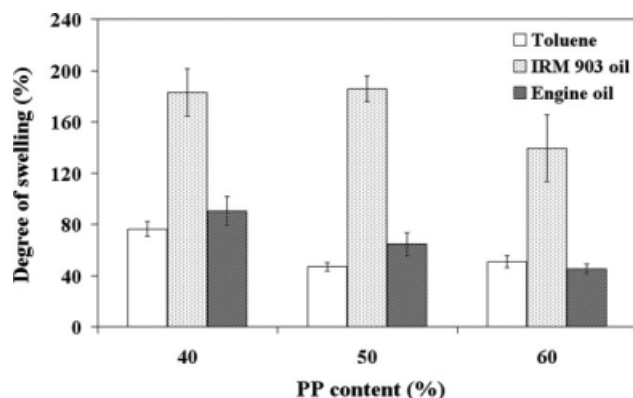


Figure 8 Degree of swelling of uTPNRs containing 40–60% PP.

mechanical properties. Chakraborty et al.² reported tension set of PP/EPDM uTPNRs containing compatibilizers. Unfortunately, they did not show tension set of the blend without the compatibilizer. High elongation at break (200–400%) and low tension set (12–22%) of the present vTPNRs reflect practical elastic properties and are appropriate for many applications such as weather strip, window seal, and appliance grip.

Results of swelling test of uTPNRs and vTPNRs were represented in Figures 8 and 9 respectively. NR in TPO was able to dissolve in toluene noticed by turbidity of solvent and changing in specimen color after testing, resulting in lower degree of swelling in TPO. After rubber vulcanization, vTPNRs showed higher resistance in toluene. uTPNRs seemed to be less resistance in IRM 903 oil. As expected, degree of swelling decreased with increasing PP content, the more NR the more swelling. Vulcanization improved oil resistance of the blend. High swelling in toluene of vTPNRs indicated crosslinks in the blends as well.

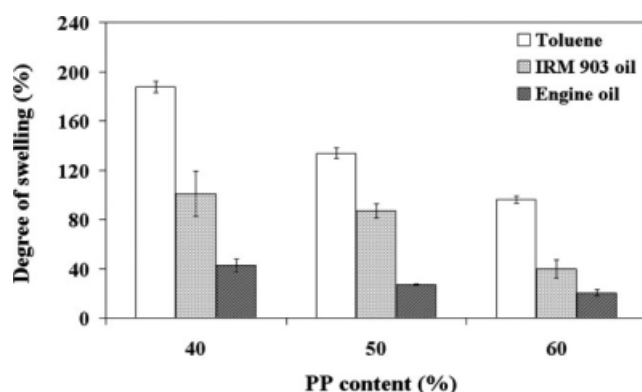


Figure 9 Degree of swelling of vTPNRs containing 40–60% PP.

TABLE VI
Changes in Tensile Properties After Thermal and Ozone Ageing of uTPNRs^a

PP (%)	Change in property after thermal ageing (%)		Change in property after ozone ageing (%)	
	σ_b	ϵ_b	σ_b	ϵ_b
40	−7.87	−32.97	−51.69	−40.86
50	+8.73	−33.48	−43.53	−37.00
60	−24.13	−23.89	−40.95	−37.54

^a Containing 40–60 wt % of PP tested at 50 mm/min.

Changes in elongation at break after thermal ageing of uTPNRs seemed to be similar for all blend compositions as shown in Table VI, but changes in tensile strength were in various different values. The positive value indicates an increase in property and *vice versa*. The tremendous increase in tensile strength after thermal ageing of TPV, as shown in Table VII, may be due to vulcanization occurring during thermal ageing. Lesser changes in elongation at break of TPV were derived. Another advantage of dynamic vulcanization was the improvement in ozone resistance as shown in Table VI and VII. It is known that NR is easily attacked by ozone due to unsaturation in the polymer backbone; consequently, crosslinked NR is essential.

Effect of reprocessing

One of the advantages of TPV is the reprocessability of this material. The method used to investigate reprocessability was mentioned by Liu et al.⁴³ Table VIII showed tensile properties of TPV containing 50% PP after reprocessing 1–3 times. Tensile strength and elongation at break decreased with reprocessing. The present vTPNR showed capability to recycle although the change in tensile properties was quite high compared to that reported in polyamide/EPDM TPV.⁴³ NR has more unsaturation than

TABLE VII
Changes in tensile properties after thermal and ozone ageing of vTPNRs^a

PP (%)	Change in property after thermal ageing (%)		Change in property after ozone ageing (%)	
	σ_b	ϵ_b	σ_b	ϵ_b
40	+76.20	+25.49	+13.84	+39.22
50	+40.98	−10.33	+5.40	+0.50
60	+55.70	−6.13	−1.48	−6.13

^a containing 40–60 wt % of PP tested at 50 mm/min.

TABLE VIII
Tensile Properties of vTPNRs^a

Number of recycle	σ_b (MPa)	ε_b (%)
0	14.64 \pm 0.53	397 \pm 31
1	11.55 \pm 1.39	345 \pm 39
2	10.24 \pm 1.40	322 \pm 61
3	10.03 \pm 1.43	290 \pm 67

^a Containing 50% PP after reprocessing tested at 50 mm/min.

EPDM; for that reason, NR faces thermal degradation more than EPDM.

CONCLUSIONS

TPEs of PP and NR with and without phenolic resins were prepared. Dynamic vulcanization with phenolic resin affected blend morphology resulting in changes in mechanical and physical properties. Phenolic resin without catalyst was able to crosslink NR during melt mixing with PP and caused NR to change from continuous phase to small particles dispersed in PP matrix. NR particle size decreased with increasing PP content were 2.13 μm , 0.88 μm , and 0.63 μm for 40, 50, and 60% PP respectively. The submicron NR particles increased tensile properties, thermal ageing resistance, ozone resistance and oil resistance compared with the TPEs containing continuous phase of NR (uTPNRs). Crosslinking in NR showed no significant effect in hardness of TPNRs and hardness increased with increasing PP content. Tension set increased with PP content and decreased remarkably after vulcanization. The present vTPNRs exhibited lower tension set compared with PP/ENR TPV. This is because of better matched polarity of blend components in PP/NR than in PP/ENR. The prepared vTPNR exhibited capability to reprocessability and tensile properties decreased after reprocessing due to polymer degradation. It should be noted that it was not necessary to add a compatibilizer in the present blends.

References

- Bhowmick, A. K.; Stephens, H. L. In *Handbook of Elastomers: New Developments and Technology*; Marcel Dekker: New York, 1988.
- Chakraborty, P.; Ganguly, A.; Mitra, S.; Bhowmick, A. K. *Polym Eng Sci* 2008, 48, 477.
- Steller, R.; Zuchowska, D.; Meissner, W.; Pauksza, D.; Garbarczyk, J. *Radiat Phys Chem* 2006, 75, 259.
- D'Orazio, L.; Mancarella, C.; Martuscelli, E.; Sticotti, G.; Ghisellini, R. *J Appl Polym Sci* 1994, 53, 387.
- Al-Malaika, S.; Amir, E. *J Polym Degrad Stab* 1986, 16, 347.
- Al-Malaika, S.; Amir, E. *J Polym Degrad Stab* 1989, 26, 31.
- Choudhury, N. R.; Chaki, T. K.; Bhowmick, A. K. *Thermochim Acta* 1991, 176, 149.
- Ismail, H.; Suryadiansyah. *Polym Test* 2002, 21, 389.
- Oh, J. S.; Isayev, A. I.; Rogunova, M. A. *Polymer* 2003, 44, 2337.
- Akhtar, S. *Euro Polym J* 1988, 24, 651.
- Choudhury, N. R.; Bhowmick, A. K. *Polym Degrad Stab* 1989, 25, 39.
- Choudhury, N. R.; Chaki, T. K.; Dutta, A.; Bhowmick, A. K. *Polymer* 1989, 30, 2047.
- Goharpey, F.; Katbab, A. A.; Nazockdast, H. *J Appl Polym Sci* 2001, 81, 2531.
- Winters, R.; Lugtenburg, J.; Litvinov, V. M.; van Duin, M.; de Groot, H. J. M. *Polymer* 2001, 42, 9745.
- Wright, K. J.; Indukuri, K.; Lesser, A. *J Polym Eng Sci* 2003, 43, 531.
- Asami, T.; Nitta, K. H. *Polymer* 2004, 45, 5301.
- Ellul, M. D.; Tsou, A. H.; Hu, W. *Polymer* 2004, 45, 3351.
- Jayaraman, K.; Kolli, V. G.; Kang, S. Y.; Kumar, S.; Ellul, M. D. *J Appl Polym Sci* 2004, 93, 113.
- Sengupta, P.; Noordermeer, J. W. M. *Polymer* 2005, 46, 12298.
- Goharpey, F.; Nazockdast, H.; Katbab, A. A. *Polym Eng Sci* 2005, 45, 84.
- Sengers, W. G. F.; Wubbenhorst, M.; Picken, S. J.; Gotsis, A. D. *Polymer* 2005, 46, 6391.
- Naskar, K.; Noordermeer, J. W. M. *J Appl Polym Sci* 2006, 100, 3877.
- Thitithammawong, A.; Noordermeer, J. W. M.; Kaesaman, A.; Nakason, C. *J Appl Polym Sci* 2007, 107, 2436.
- Lei, C.; Huang, X.; Ma, F. *Polym Advan Technol* 2007, 18, 999.
- Nakason, C.; Wannavilai, P.; Kaesaman, A. *Polym Test* 2006, 25, 34.
- George, S.; Ramamurthy, K.; Anand, J. S.; Groeninckx, G.; Varghese, K. T.; Thomas, S. *Polymer* 1999, 40, 4325.
- Soares, B. G.; Almeida, M. S. M.; Urs, M. V. D.; Kumaraswamy, G. N.; Ranganathaiah, C.; Siddaramaiah; Mauler, R. *J Appl Polym Sci* 2006, 102, 4672.
- Soares, B. G.; Almeida, M. S. M.; Ranganathaiah, C.; Urs, M. V. D.; Siddaramaiah. *Polym Test* 2007, 26, 88.
- Fritz, H. G.; Bolz, U.; Cai, Q. *Polym Eng Sci* 1999, 39, 1087.
- Pesneau, I.; Champagne, M. F.; Huneault, M. A. *Polym Eng Sci* 2002, 42, 2016.
- Kuriakose, B.; Chakraborty, S. K.; De, S. K. *Mater Chem Phys* 1985, 12, 157.
- Kuriakose, B.; De, S. K. *Polym Eng Sci* 1985, 25, 630.
- Kuriakose, B.; De, S. K.; Bhagawan, S. S.; Sivaramkrishnan, R.; Athithan, S. K. *J Appl Polym Sci* 1986, 32, 5509.
- Varghese, S.; Alex, R.; Kuriakose, B. *J Appl Polym Sci* 2004, 92, 2063.
- Thitithammawong, A.; Nakason, C.; Sahakaro, K.; Noordermeer, J. *Polym Test* 2007, 26, 537.
- Nakason, C.; Saiwari, S.; Kaesaman, A. *Polym Eng Sci* 2006, 46, 594.
- Akhtar, S.; De, P. P.; De, S. K. *Mater Chem Phys* 1985, 12, 235.
- Akhtar, S.; De, P. P.; De, S. K. *Mater Let* 1988, 6, 186.
- Bhowmick, A. K.; Heslop, J.; White, J. R. *Polym Degrad Stab* 2001, 74, 513.
- Bhowmick, A. K.; Heslop, J.; White, J. R. *J Appl Polym Sci* 2002, 86, 2393.
- Nakason, C.; Nuansomsri, K.; Kaesaman, A.; Kiatkamjornwong, S. *Polym Test* 2006, 25, 782.
- Ward, I. M.; Hadley, D. W. *An Introduction to the Mechanical Properties of Solid Polymers*; Wiley: New York, 1995.
- Liu, X.; Huang, H.; Sie, Z. Y.; Zhang, Y.; Zhang, Y. X.; Sun, K.; Min, L. N. *Polym Test* 2003, 22, 9.