

Development and Preparation of High-Performance Thermoplastic Vulcanizates Based on Blends of Natural Rubber and Thermoplastic Polyurethanes

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ABSTRACT: Natural rubber (NR)/thermoplastic polyurethane (TPU) blends were prepared with a dynamic vulcanization technique. The main objective was to prepare high-performance thermoplastic vulcanizates (TPVs) based on natural rubber [thermoplastic natural rubber (TPNR)] with low hardness values and improved thermal and mechanical properties. In this study, the preparation of dynamically cured NR/TPU blends was carried out systematically, and the final properties were compared to those of typical commercial TPVs. The influence of sulfur-cured systems, accelerator types, process parameters, and rubber types were investigated. The developed NR/TPU-based TPNRs showed better tensile strengths and thermal properties than commercial TPVs with similar hardnesses. Moreover, the epoxidized natural rubber (ENR)/TPU-based TPNRs exhibited a low compression set. The incorporation of NR into the TPU reduced the Shore A hardness to about 60 in comparison to a value of about 85 for the neat TPU; the blends also showed improved oil resistance (oil swelling = 12%) in comparison to commercial TPVs with similar hardnesses. The experimental results indicate that high-performance TPNRs with low hardness values could be prepared with the proper conditions developed in this study. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Thermoplastic elastomers (TPEs) are a class of materials that combine the properties of conventional rubbers and the processability of thermoplastics. A further advantage is that production scraps and waste can be recycled.¹ One important group of TPEs is the blends of thermoplastic polymers and rubber. There are two main classes of TPE materials based on the blending technique: simple blends and dynamic vulcanizates. Simple blends are prepared by the mixture of polymer pairs without curatives to obtain a co-continuous phase morphology. Dynamic thermoplastic vulcanizates (TPVs) are blends of rubber and thermoplastic polymers in which the rubber phase is dynamically crosslinked during the melt-blending process. The final morphology of a dynamically vulcanized blend has dispersed vulcanized rubber domains in the thermoplastic matrix.² The technology of dynamic vulcanization has been commercialized successfully. Today, these materials are the most interesting subgroup of TPEs. TPVs play an important role in the materials

industry and are among the fastest growing sector of the polymer market. Almost all commercial TPVs are based on synthetic polymers, especially ethylene–propylene diene rubber (EPDM) and polypropylene (PP). TPVs based on EPDM/PP exhibit only moderate heat resistance and poor oil resistance. Engineering thermoplastic vulcanizate (ETPV) or super TPV products were recently introduced to the polymer market. Most are based on a combination of high-performance polar synthetic rubbers, such as acrylic rubber (ACM) or ethylene-acrylic rubber (AEM), in polar thermoplastic matrix polymers (e.g., polyesters and polyamides) to achieve better heat and oil resistance. However, the production expenses of these materials are high, and further improvement of the mechanical properties is desired. Natural rubber (NR) is the most important polymer basis of thermoset rubber, and it covers a wide variety of applications. Furthermore, NR can be considered one of the most important natural polymers; it is renewable and ecofriendly. Therefore, the development of thermoplastic natural rubber (TPNR) has attracted

scientific interest. TPNRs are a special group of TPVs in which a vulcanized NR as the elastomeric phase is dispersed in a thermoplastic polymer matrix. TPNRs offer several benefits; in particular, they exhibit the processability of thermoplastics. The use of renewable and ecofriendly polymers, such as NR, as the main component of these blends helps to preserve resources and, thus, contributes to the sustainable development of new products. TPNRs are environmentally friendly materials and have high potential in the polymer industry. Thermoplastic polyurethane (TPU) has been recognized as a material with excellent oil and aging resistance and superior mechanical properties; nevertheless, it suffers from inferior elasticity and damping properties. The blending of TPU with NR could provide materials with a higher elasticity and better damping properties. Furthermore, this type of blend uses halogen-free materials and could be used in many applications, to substitute poly(vinyl chloride). However, the blending of NR with high-melting-temperature thermoplastics, such as TPU, remains a challenge because the degradation temperature of NR is lower than the melting temperature of TPU; this leads to deteriorations in the mechanical properties of the final blends.³ Because of this, the processing conditions are vital to controlling and limiting the degradation of NR during its blending with thermoplastics.

In this study, we attempted to prepare TPVs based on blends of NR and TPU with a dynamic vulcanization process. The aim of this study was to develop and characterize high-performance TPVs of low Shore A hardness (~ 60) based on NR. These TPVs based on NR/TPU blends were expected to have improved performance over existing commercial or typical TPV products in addition to their environmental sustainability benefits. The influences of different sulfur cure systems, accelerator types, and mixing process parameters on the mechanical, thermal, and oil resistance properties of the TPVs were systematically studied. Furthermore, the goal of this study was to examine the effects of different levels of modification by epoxide groups of the NR on the final properties of the TPVs.

EXPERIMENTAL

Materials

NR as air-dried sheets was manufactured by the Khuan Pun Tae Farmer Corp. (Phattalung, Thailand). High-ammonia NR latex with a dry rubber content of approximately 60 wt %, manufactured by the Rubber Estate Organization (Nakorn Sri Thammarat, Thailand), was used as the raw material for the preparation of epoxidized natural rubber (ENR). ENRs, with levels of 25 and 50 mol % epoxide groups, were prepared in-house via performic epoxidation with formic acid and hydrogen peroxide, as described in our previous article.⁴ Both epoxidation reagents were supplied by Riedel-de Haen (Seelze, Germany). The molar contents of the epoxide groups in the NR molecules⁵ were determined by means of ¹H-NMR spectroscopy. The calculation was based on the integrated area under the peak assigned to oxirane protons in the ENR. TPU, Elastollan C 85A (Elastogran GmbH, Lemförde, Germany), was used as the matrix component. Sulfur was used as the vulcanizing agent and was obtained from H. M. Royal, Inc. (NJ). Zinc oxide and stearic acid were

used as activators and were obtained from Lanxess GmbH (Leverkusen, Germany) and Unichema International B. V. (Gauda, The Netherlands), respectively. Benzothiazyl-2-cyclo-hexyl sulfonamide (DCBS), *N*-tert-butyl-2-benzothiazole sulfenamide (TBBS), *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS), and tetramethyl thiuram disulfide (TMTD), acting as accelerators, were obtained from Lanxess. Furthermore, Wingstay L, from Eliokem, Inc. (OH), was used as an antioxidant.

Preparation of TPVs Based on NR/TPU Blends

Influence of the Sulfur Curing Systems on the Properties of the Dynamically Cured NR/TPU Blends. To select the optimal curing system, experiments with a conventional vulcanization (CV) system, semiefficient vulcanization (SEV) system, and efficient vulcanization (EV) system were prepared. The accelerator-to-sulfur ratios were 1 : 7, 1 : 1, and 7 : 1 phr in the CV, SEV, and EV systems, respectively. The premasticated NR was mixed with stearic acid, ZnO, TBBS, and sulfur. The total mixing time was 9 min at a chamber temperature of 60°C. The final compound temperature was approximately 90°C. The compound was formed into a sheet 2–3 mm in thickness and left to cool at room temperature. The scorching time (t_{s1}) and curing time (t_{90}) were measured at 180°C with a dynamic moving die rheometer (D-MDR 3000, MonTech, Buchen, Germany). The rubber compounds were later dynamically cured during blending with TPU in an internal mixer (Haake Rheocord 600, Thermo Electron Corp., Karlsruhe, Germany) with a mixing capacity of 80 cm³. The blend ratio of NR to TPU was fixed at 40 : 60. The TPU was dried before the mixing process at 60°C in a hot-air oven for at least 10 h to remove moisture. Three different NR compounds with the CV, SEV, and EV systems were used, and their influences on the properties of the TPVs were studied. The mixing process started with the heating of the TPU in the mixing chamber at 200°C for 5 min without rotation; this was followed by mixing in the NR compound at a rotor speed of 60 rpm at about 200°C for 10 min. The products were cooled down to room temperature and cut into small pieces. Test specimens of the TPVs were prepared with a manual injection-molding press (Ray-Ran Test Equipment, Ltd., Warwickshire, United Kingdom).

Influence of the Accelerator Type on the Properties of the Dynamically Cured NR/TPU Blends. In this part of the study, NR compounds with various accelerator types (i.e., TBBS, CBS, TMTD, mixed TBBS/TMTD, and DCBS) were prepared with the formulations given in Table I. The same blend ratio and mixing conditions described previously were used.

Optimization of the Processing Parameters for the Production of the Dynamically Cured NR/TPU Blends. In this part, the NR was compounded with the most suitable curing system and accelerator type, as found in the first and second part of this work, to study the influence of the processing parameters on the properties of the TPVs. The rubber compounds were dynamically cured during blending with TPU in an internal mixer. The maximum chamber temperature, mixing time, and rotor speed were varied, as shown in Table II. All other parameters were held constant. The mechanical properties of the TPVs,

Table I. Compounding Formulation of NRs with Various Accelerator Types for the Preparation of the Dynamically Cured NR/TPU Blends

Ingredient	Quantity (phr)				
	TBBS	CBS	TMTD	Mixed (TBBS/TMTD)	DCBS
NR	100	100	100	100	100
Stearic acid	0.5	0.5	0.5	0.5	0.5
ZnO	2.0	2.0	2.0	2.0	2.0
TBBS	3.5	—	—	2.5	—
CBS	—	3.5	—	—	—
TMTD	—	—	4.0	1.0	—
DCBS	—	—	—	—	3.5
Sulfur	0.5	0.5	—	0.5	0.5
Wingstay L	1.0	1.0	1.0	1.0	1.0

in particular, the tensile strength, were used to determine the preferred processing parameters.

Influence of the Rubber Type on the Properties of the Dynamically Cured NR/TPU Blends. The ENRs (i.e., ENR-25 and ENR-50) were compounded with the formulations shown in Table III. Unmodified NR was also compounded for comparison purposes. The rubber compounds were later dynamically cured during blending with TPU in an internal mixer with the most suitable processing parameters. Blending was performed at a rotor speed of 100 rpm and at a temperature of $\sim 190^\circ\text{C}$ for 6 min. To determine the mechanical properties, oil resistance, and thermal stability, suitable test specimens of the TPVs were prepared by injection molding.

Testing and Characterization

Tensile and Hardness Tests. Tensile testing of dumbbell-shaped specimens (type 5A) was performed at $23 \pm 2^\circ\text{C}$ according to ISO 527 with a Zwick Z 1545 tensile testing machine (Zwick GmbH & Co., Ulm, Germany) at a fixed extension speed of 200 mm/min. The hardness of materials was tested with a Shore A durometer (Frank GmbH, Hamburg, Germany) according to ISO 868.

Temperature-Scanning Stress-Relaxation (TSSR) Measurement. The TSSR method is based on a stress-relaxation test, which is conducted under nonisothermal conditions. In this work, TSSR was used to evaluate the relaxation behavior and thermoelastic properties of the TPVs. The TSSR measurement was performed with a commercially available TSSR instrument of Brabender GmbH (Duisburg, Germany). During the TSSR test, a constant tensile strain of 50% was applied to a dumbbell test piece (type 5A, ISO 527). After the strain was applied, the sample was preconditioned at 23°C for 2 h without heating. Subsequently, the sample was heated at a rate of $2^\circ\text{C}/\text{min}$ until the stress relaxation was fully complete or until the sample failed. With the fixture gap kept constant during the entire test, the results were plotted as force (F)–temperature curves. Some characteristic values of the samples, such as T_{10} , T_{50} , T_{90} , and TSSR index [or rubber index (RI)], were obtained, where T_x stands for the temperature at which F decreased by x percent

Table II. Mixing Method Schedule for the Preparation of the TPVs through the Variation of the Three Mixing Parameters

Mixing parameter	Method A	Method B	Method C
Temperatures ($^\circ\text{C}$) ^a	183, 189, 195, and 205	~ 200	~ 200
Times (min)	10	2, 6, 10, and 15	10
Rotor speeds (rpm)	60	60	40, 60, 100, and 160

^aMaximum temperatures during the blending process.

from the initial force (F_0). The temperatures T_{10} , T_{50} , and T_{90} are in common use as material characteristics. T_{10} ^{6,16} describes the temperature at which the stress-relaxation processes compensated for the elastic stress increase by entropy, whereas T_{50} can be considered the upper limit of the service temperature range. At temperatures higher than T_{90} , viscous flow becomes the dominant relaxation process; this is caused by the melting or softening of the hard phase. Thus, T_{90} served as a measure of the thermal resistance of the tested material.¹⁷

The TSSR index, or RI, is a measure of the rubberlike behavior of the material. For this, the area below the normalized (F/F_0) F –temperature curve was determined between the starting temperature (T_0) and the temperature limit (T_{90}) and was expressed as fraction of the area of a rectangle with width ($T_{90} - T_0$) and the height of F_0/F_0 . This rectangle represented the behavior of an idealized elastomeric material that did not show any decrease in stress over the observed temperature range; such an ideal material would have $\text{RI} = 1$, whereas the determined values remained less than this. The higher the value of RI was, the more rubberlike was the behavior of the examined material. RI was calculated according to eq. (1)⁶:

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

where $F(T)$ is the force at the testing temperature (T), F_0 is the initial force determined at the starting temperature (T_0), and

Table III. Compounding Formulation of NRs with Different Types of Rubber for the Preparation of the Dynamically Cured NR/TPU Blends

Ingredient	Quantity (phr)		
	Unmodified NR	ENR-25	ENR-50
Unmodified NR	100	—	—
ENR-25	—	100	—
ENR-50	—	—	100
Stearic acid	0.5	0.5	0.5
ZnO	2.0	2.0	2.0
DCBS	3.5	3.5	3.5
Sulfur	0.5	0.5	0.5
Wingstay L	1.0	1.0	1.0

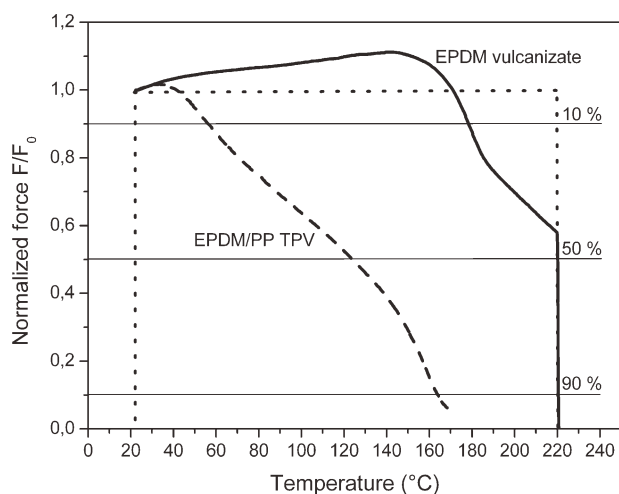


Figure 1. Normalized F -temperature curves of the (—) EPDM vulcanizate and (---) dynamically cured EPDM/PP blend obtained from the TSSR measurement.⁶

T_{90} is the temperature at which F decreased about 90% with respect to F_0 .

In a previous study, it was shown that from the initial part of the stress-temperature curve, additional information about the structure of the material could be deduced. As shown in Figure 1, the stress increased almost linearly with temperature in the case of conventional vulcanized rubber. This was due to the entropic effect, which is well known in the theory of rubber elasticity.

From the TSSR measurements, the temperature coefficient (κ) of stress could be calculated according eq. (2):

$$\kappa = (\partial\sigma/\partial T)_{\lambda,\rho} \quad (2)$$

Where σ is the stress, λ is the strain ratio and ρ is the ambient pressure. According to theory of ideal rubber networks, κ is correlated with the crosslinking density, but in the case of more complex real vulcanizates, κ is also influenced by other factors, such as the polymer-filler interactions.⁷ The entropic effect was also recognizable from Figure 1 for TPV but only in the initial part of the curve. After exceeding a certain relatively low temperature, the entropic effect was overcompensated by stress relaxation because of the fact that the thermally reversible physical crosslinks could be untied at these temperatures.

The slope of the increasing stress corresponded to the crosslinking density⁶ and/or the interaction between both phases⁸ in those materials. For TPV, the entropic effect, therefore, is an important phenomenon related to the interactions of the blend components.

Compression Set and Oil-Swelling Tests. The determination of the compression set is a method used to measure the elastomeric properties of rubbery materials, in particular, TPVs. These tests were conducted with a compressive strain of 25% in accordance with ISO 815 at a temperature of 100°C for a period of 24 h and for a subsequent relaxation time of 30 min. Oil-swelling tests were performed at 150°C for 70 h by use of squarely shaped test pieces with size of 100 mm² and a thickness of 2 mm. The degree of swelling was calculated from the mass change of the specimen

before and after immersion in the test liquid. In this work, engine oil (SAE 20 W-50 motor oil, Shell Deutschland Oil GmbH, Hamburg, Germany) was used as a test liquid.

Morphological Characterization. Morphological characterization was performed with atomic force microscopy (AFM; Nanosurf EasyScan 2 AFM, Nanosurf AG, Liestal, Switzerland). AFM was used to visualize the surface topology at room temperature in tapping mode with a cantilever nanosensor of type NCLR (non-contact long cantilever with reflex coating) with a typical static load of 10 nN at a dynamic frequency of 190 kHz. The samples were first cut with a metal blade under cryogenic conditions at -100°C to prepare a smooth surface before they were examined with AFM.

RESULTS AND DISCUSSION

Influence of the Sulfur Curing Systems on the Properties of the Dynamically Cured NR/TPU Blends

Initially, we faced difficulties in the processability of the TPVs with respect to injection-molding; these may have been caused by inappropriate curing of the NR phase during the preparation of the dynamically cured NR/TPU blends, and thus, incomplete curing, overcuring, or degradation of the NR phase was occurring. Therefore, the curing kinetics of NR and its effect on properties of the TPVs were studied first to understand the processability and other properties. The relationship between the stress and strain of the TPVs for different cure systems is shown in Figure 2. It can be seen that the TPV prepared with the EV curing system exhibited the highest tensile strength. On the other hand, the CV curing system resulted in the lowest tensile strength and elongation at break, whereas the TPV containing the SEV system showed a medium tensile strength but the highest elongation at break. It is well known that the EV system is thermally more stable than the SEV and CV systems. Therefore, the mechanical properties of the NR blends were expected to follow the trend of thermostability of the curing systems, as observed: EV > SEV > CV. Figure 3 shows the curing curves of the NR premixtures prepared by the use of the three different curing systems (i.e., CV, SEV, and EV). The curing characteristics of the NR compounds

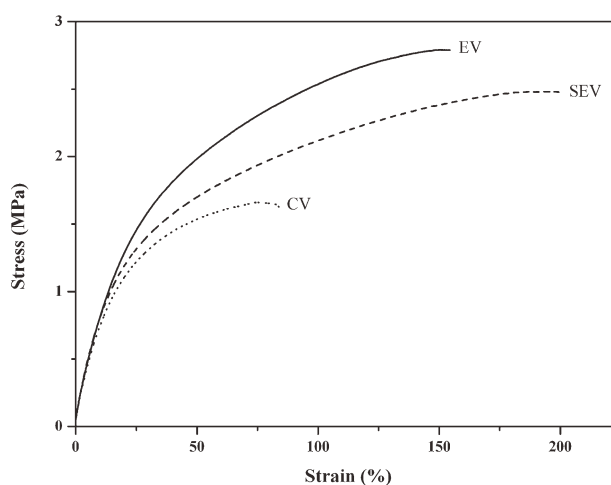


Figure 2. Stress-strain curves of NR/TPU TPVs with different curing systems: (· · ·) CV, (---) SEV, and (—) EV.

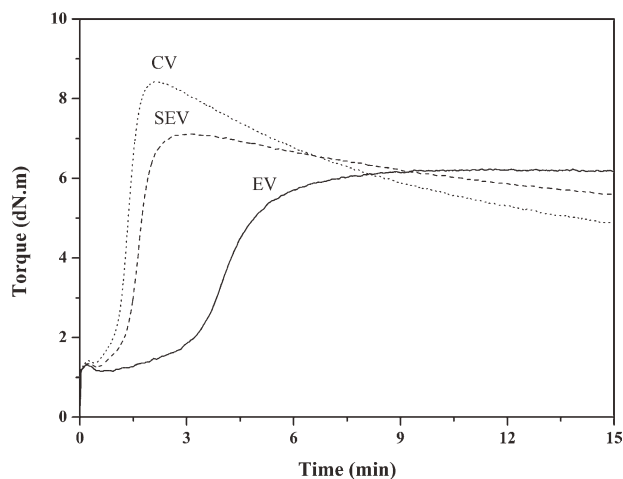


Figure 3. Curing curves of NR compounds with different curing systems at 180°C: (· · ·) CV, (– –) SEV, and (—) EV.

were examined at 180°C for 15 min. The curing curves for the NR compounds with the CV and SEV curing systems showed strong and slight reversions, respectively. The later, where the torque decreased after it reached a maximum, was caused by the loss of crosslinking structure to thermal degradation. In contrast, the NR compound with the EV system showed a curing curve that plateaued. Thereby, under the high-temperature conditions during the dynamic vulcanization process, the EV system was found to be the most suitable curing system for the rubber phase and was used for the rest of this study.

Influence of the Accelerator Type on the Properties of the Dynamically Cured NR/TPU Blends

As described before, the EV curing system provided TPVs with better tensile strengths than the SEV and CV curing systems. So, the EV system was selected and used for the preparation of the TPVs while the type of accelerator was varied. Table IV shows the t_{s1} , t_{90} , and changes in torque, i.e. maximum torque MH minus minimum torque ML, of compounds containing various types of accelerator. It was found that the NR compounded with DCBS showed the longest t_{90} (13.6 min) and a reasonable t_{s1} (3.0 min). The t_{90} values with the other types of accelerators (i.e., TBBS, CBS, TMTD, mixed TBBS/TMTD) were shorter. The TBBS and CBS compounds exhibited t_{s1} values similar to the DCBS compound, but the TMTD and mixed TBBS/TMTD compounds showed much shorter t_{s1} values. It can also be seen from Table IV that the compound containing mixed accelerator

(TBBS/TMTD) showed the highest change in torque (MH – ML) because of a synergistic effect. Obviously, the five types of accelerators of the curing reaction in the NR compounds exhibited different curing behaviors; this directly affected the properties of the TPVs. The use of DCBS provided TPVs with the highest tensile strength. According to these results, the accelerator effect on the tensile properties could be ranked from high to low as follows: DCBS > TBBS > CBS > Mixed TBBS/TMTD > TMTD. From comparison of the t_{s1} values of the rubber compounds and the tensile strengths of the TPVs compiled in Table IV, we could see that the tensile strengths of the TPVs correlated well with the t_{s1} values of the rubber compounds. Presumably, the development of the morphology of the TPVs was strongly influenced by the initial formation of a cocontinuous phase morphology.⁹ Under continuous shearing stress at a high temperature, the nonvulcanized rubber phase turned into vulcanized rubber particles; when t_{s1} of the rubber compound was short, the vulcanization kinetics outpaced particle dispersion, and this led to fewer dispersed NRs and a large particle size (see Figure 4). To achieve an NR/TPU system with well-dispersed small rubber particles, a sufficiently long t_{s1} was needed to allow rubber-phase breakup before vulcanization, as seen in the DCBS-containing system. This was corroborated by the relationship between the tensile strength of the TPVs and the t_{s1} of the rubber compounds. It was observed that the tensile strength of the TPVs increased with increasing t_{s1} . This mechanistic explanation was also supported by a basic relationship between the particle size of the rubber domains and the stress-strain properties of the TPVs,¹⁰ from which it is known that the tensile strength increased with decreasing particle size of the rubber domains in the matrix. Although, according to the change in torque (MH – ML) results, DCBS apparently had the lowest crosslink density (MH – ML), it provided the highest tensile strength to the TPVs. We concluded that, t_{s1} of the rubber compound was one of the most important factors affecting the properties of the TPVs. Consequently, an EV curing system with DCBS as the accelerator, based on the properties of TPV, was selected and is discussed in the next section.

Optimization of the Processing Parameters

The conditions of mixing during the dynamic vulcanization process are known to be most important for the morphology of TPVs. Therefore, optimization of the mixing parameters was needed to further improve the properties of the TPVs. NR is well known for its high sensitivities to heat and oxidation, which are caused by the unsaturation of the polymer backbone. Hence, the

Table IV. Curing Characteristics at 180°C, Tensile Strength, and Elongation at Break of the NR Compounds with Different Accelerator Types with the EV System

Accelerator type	MH – ML (d Nm)	t_{s1} (min)	t_{90} (min)	Tensile strength (MPa)	Elongation at break (%)
TBBS	5.3	2.8	5.0	2.4 ± 0.7	133 ± 28
CBS	5.1	2.4	4.2	1.9 ± 0.3	89 ± 6
TMTD	4.2	0.7	1.7	1.0 ± 0.5	35 ± 10
Mixed (TBBS + TMTD)	5.6	1.0	1.8	1.4 ± 0.1	91 ± 3
DCBS	3.0	3.0	13.6	2.7 ± 0.2	272 ± 3

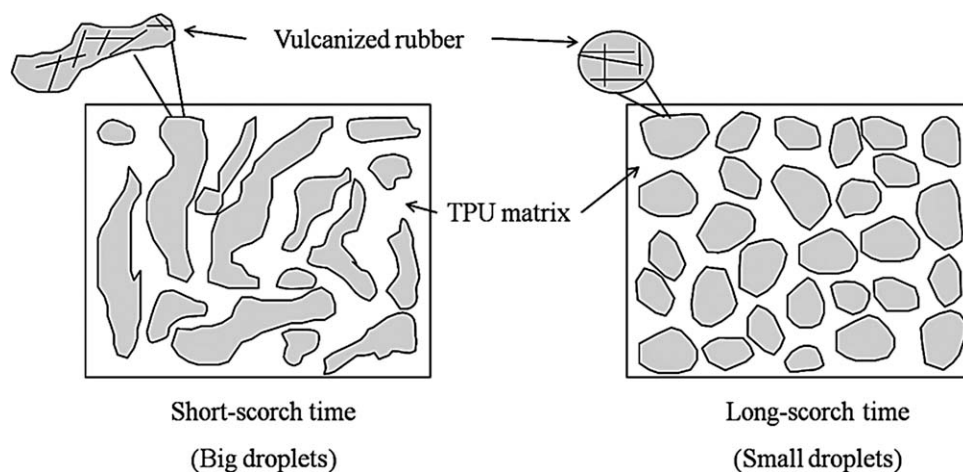


Figure 4. Proposed model of the morphologies of TPVs with NRs with different t_{s1} values.

NR phase degraded at a high melting temperature combined with shear stress during the mixing stage of the preparation of the dynamically cured TPVs. However, it was very difficult to prevent the deleterious conditions because a high processing temperature was needed to melt the thermoplastic matrix polymer. Also, a high shear stress was needed to disperse and reduce the size of the NR particles in the thermoplastic matrix. The mixing parameters (i.e., temperature, time, and rotor speed) affected the final properties of the TPV and were needed for balance between competing phenomena, as schematically illustrated in Figure 5. It was clear that all of the mixing parameters strongly affected the final properties of the NR/TPU TPVs and that, for each there,

may have been an optimal setting between the negative effects encountered at the extremes. The effects of these parameters were evaluated by experiments in each of which two of the parameters were fixed and the third parameter was varied systematically (methods A, B, and C), as summarized in Table II. Figure 6(A–C) shows the tensile strengths of the TPVs prepared from mixing methods A, B, and C. We found that the tensile strength decreased with increasing mixing temperature and mixing time. This was due to the higher degradation of the NR phase, which occurred during the mixing process. Notwithstanding, extremely low mixing temperatures could not be used because the mixing temperature had to be higher than the melting temperature of

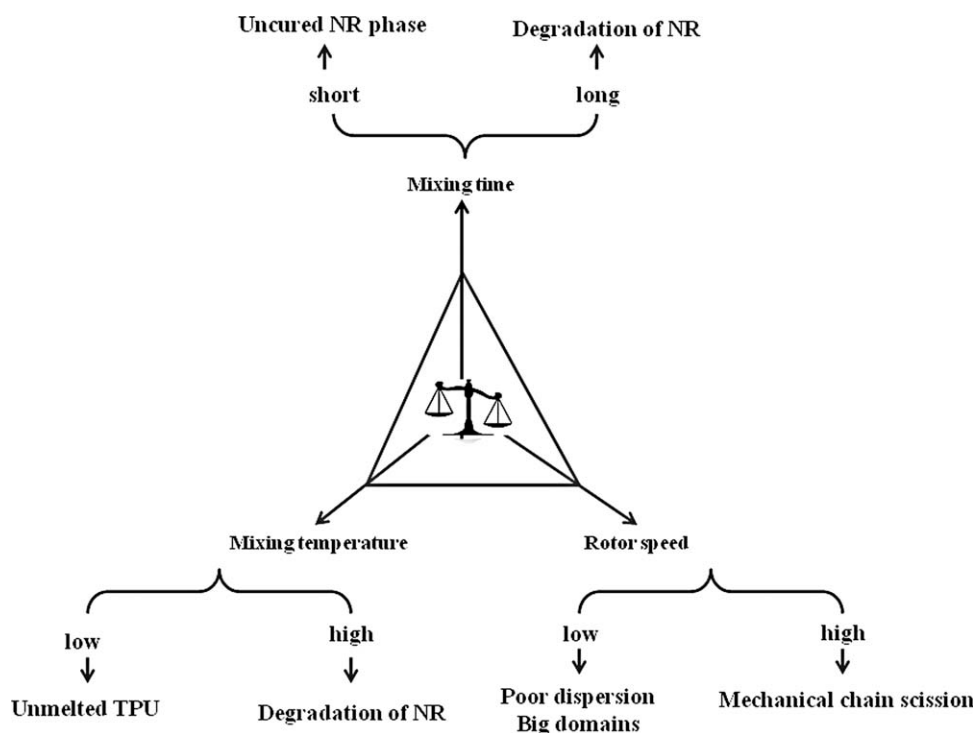


Figure 5. Expected effects of the three mixing parameters (i.e., mixing time, mixing temperature, and rotor speed) on the components and structure of the dynamically cured NR/TPU.

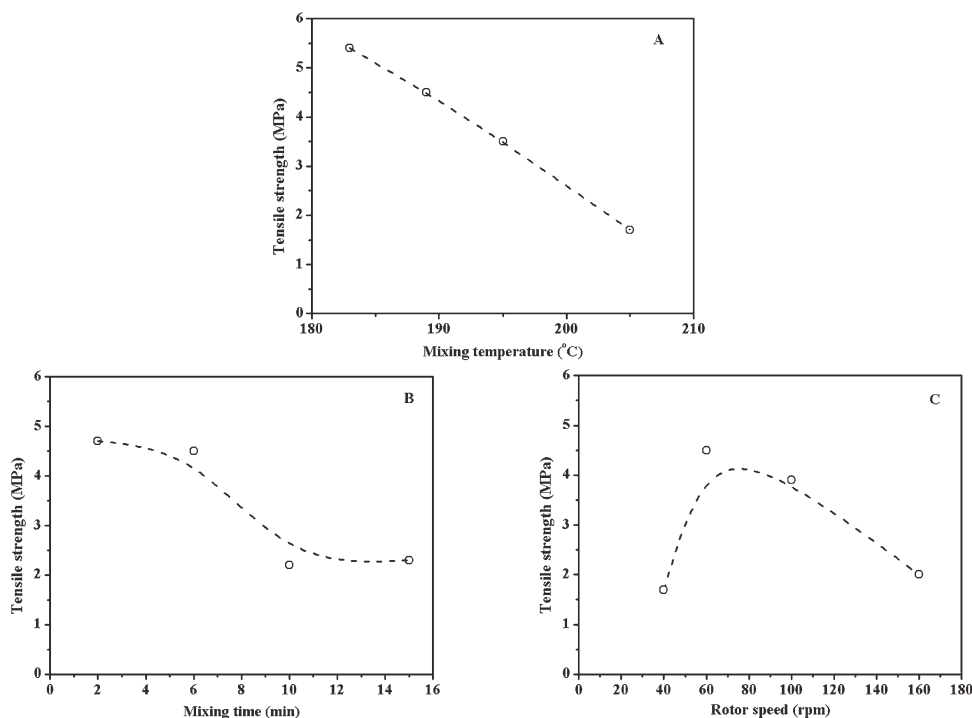


Figure 6. Tensile strength of NR/TPU TPVs with various mixing parameters: (●) mixing temperature, (◆) mixing time, and (▲) rotor speed.

TPU at about 180°C. Another important parameter was the rotor speed, which was directly related to the shear stress, and thus, strongly affected the morphology of the blends. We found that the tensile strength increased initially with increasing rotor speed. After it reached a maximum value at about 100 rpm, a decreasing trend was observed at higher rotor speeds. These results were in good agreement with the chart shown in Figure 5, which summarizes the expected effects of the mixing parameters. An extremely high shear stress during the preparation of the TPVs led to a considerable mechanical degradation of the NR phase because of high chain scission. On the other hand, a low shear stress gave poor properties because the rubber particle size was not reduced sufficiently and the rubber phase was not well distributed in the TPU matrix. Instead, large particles were formed and were poorly dispersed. Obviously, the three mixing parameters were very important for achieving the desired properties in the TPVs. The tensile strength of the TPVs were improved from about 2.5 to about 5 MPa by optimization of the mixing parameters. Even though all of the experiments were carried out with the same recipe, same ingredients, same raw materials, same chemical quality, and same mixer equipment, the properties of the TPVs were varied dramatically through the adjustment of the mixing parameters. We concluded that the optimization of processing parameters was a key factor in controlling the properties of the TPVs. The remaining experiments were carried out with optimized mixing parameters, that is, a rotor speed of 100 rpm, a mixing temperature of 190°C, and a mixing time of 6 min.

Influence of the Rubber Type on the Properties of the TPVs Based on the NR/TPU Blends

According to our previous work,^{8,11,12} ENR with 50 mol % epoxide groups (i.e., ENR-50) gave dynamically cured ENR/PA-

12 and ENR/TPU with superior mechanical properties and fine spherical grains of vulcanized rubber as the dispersed phase. In this work, ENR-25 and ENR-50 were, therefore, dynamically cured during blending with TPU. The aim was to improve the compatibility between the rubber and matrix phases. Figure 7 shows the stress–strain behavior of the dynamic vulcanizates (TPVs) prepared with the three different types of rubber: unmodified NR, ENR-25, and ENR-50. The modulus and tensile strength increased with increasing concentration of epoxide groups grafted onto the NR molecules, whereas the elongation at break remained nearly unaffected at about 350%. The thermomechanical properties were also measured with the TSSR technique. The TSSR results of the same compounds, as

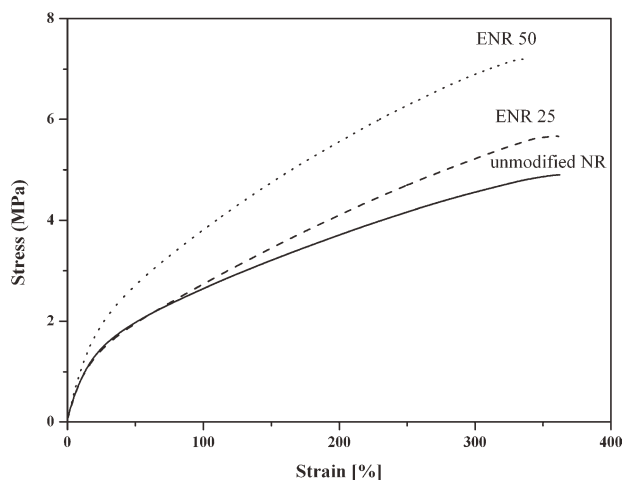


Figure 7. Stress–strain curve of NR/TPU TPVs with different NR types: (—) unmodified NR, (---) ENR-25, and (···) ENR-50.

Table V. TSSR Results of TPVs Containing Different Rubber Types

TPV sample	σ_0 (MPa)	Temperature ($^{\circ}\text{C}$)			TSSR index (RI)	κ (MPa/K)
		T_{10}	T_{50}	T_{90}		
Unmodified NR/TPU	0.9	34.8	74.7	142.8	0.50	0.8×10^{-3}
ENR-25/TPU	0.8	41.8	88.1	149.4	0.55	1.7×10^{-3}
ENR-50/TPU	0.9	50.9	102.0	163.3	0.59	3.6×10^{-3}

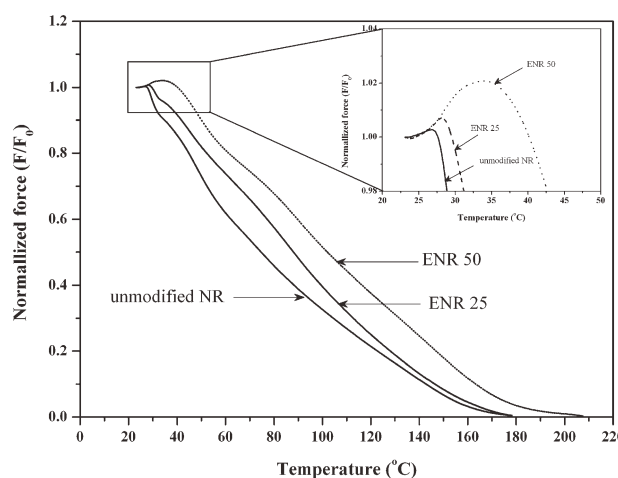
presented in Figure 7, are shown in Table V. A similar trend for the tensile properties was found. The thermomechanical properties also improved with increasing concentration of epoxide groups on the NR chain. In particular, the T_{50} value increased from about 75 to 102°C , and κ increased by a factor of more than 4 from 0.8 to 3.6 kPa/K. These characteristics indicated a clear improvement in the elastic behavior. Therefore, the trends of the tensile and thermomechanical properties of the TPVs with various types of NR were ranked as follows: ENR-50/TPU > ENR-25/TPU > Unmodified NR/TPU. This might have been due to an increase in the surface energy between the interface of the TPU and ENR phases with increasing levels of epoxide groups. That is, the polar parts of TPU (i.e., the ester in the soft segment and/or urethane groups in the hard segment) interacted with the polar groups of the ENR molecules. Moreover, the vulcanized rubber network of ENR with a higher content of epoxide groups was stronger because of the higher interaction within and between the ENR molecules via the polar groups. Therefore, increasing the number of epoxide groups in the ENR molecules also increased the mechanical strength. This mechanism was in good agreement with the observed entropic effect (from the TSSR results) of the TPVs, as shown in Figure 8. The maximum slope (κ) in the initial part of the curve and the TSSR index (RI) of the TPVs prepared with various types of NR showed a slightly increasing trend with increasing levels of epoxide groups in the ENR molecules. This trend also agreed with our previous observations.¹² Because of the many possible ways in which ENR could react with TPU, we propose to extend this study with research into such chemical reactions. Figure 9 shows the AFM micrographs of the TPVs obtained from unmodified NR/TPU and ENR-50/TPU. The ENR-50/TPU blend exhibited a finer grained morphology than the unmodified NR/TPU blend. Primarily, this was attributed to the better compatibility of ENR and TPU because the compatibility between pairs of polymers in a blend is determined by two main factors, the Gibbs free energy of mixing and possible specific intermolecular chain interactions.¹³ In the case of polymers of high molar mass, the Gibbs free energy of mixing is dominated by the heat of mixing. The degree of compatibility can also be predicted by the Flory–Huggins interaction parameter, which is closely related to the heat of mixing. According to the theoretical approach of Hildebrand,¹⁴ the Flory–Huggins interaction parameter is deduced from the difference between the solubility parameters (δ_A and δ_B) of blend components A and B. For good compatibility, the difference between δ_A and δ_B should be small. For a typical polyester-based TPU, values of δ_A and δ_B of 19.4 (J/cm^3)^{1/2} and 23.5 (J/cm^3)^{1/2}, respectively, were reported in the literature¹³ for the soft and hard segments,

respectively. Furthermore, the solubility parameters of NR and ENR with 50 mol % epoxide groups are reported as about 16 (J/cm^3)^{1/2} and 18.6 (J/cm^3)^{1/2}, respectively.¹⁵ Consequently, ENR was supposed to be better compatible with the soft segments of TPU and provided a finer grained morphology than the unmodified NR.

In addition, specific physical intermolecular chain interactions between the polar functional groups of ENR and TPU promoted the formation of a finer grain morphology. Even chemical interaction between the phases of ENR and TPU might have been possible. This topic will be a subject of further investigations. Furthermore, the higher viscosity of ENR led to a higher shear stress during the mixing process. This effect also promoted good dispersion of the ENR droplets in the TPU matrix. In conclusion, smaller ENR droplets led to an increase in the surface area of the dispersed phase and, thus, to better mechanical properties. This correlated well with the results of the tensile tests (Figure 7) and TSSR measurements (Figure 8 and Table V).

Overall Properties of the Optimized TPV Based on Dynamically Cured ENR/TPU

Table VI shows the overall properties of the optimized TPV. In comparison to other commercial available TPVs of similar Shore A hardness (~ 60 to 70), the mechanical properties of the TPV prepared in this study exhibited better results than ETPV. A T_{50} slightly above 100°C as obtained from the TSSR measurements was observed for the optimized TPV based on ENR/TPU, whereas the ETPVs showed a lower value of about 96°C . On the other hand, in comparison to those of a typical EPDM/

**Figure 8.** TSSR curves of NR/TPU TPVs with different NR types: (—) unmodified NR, (---) ENR-25, and (···) ENR-50.

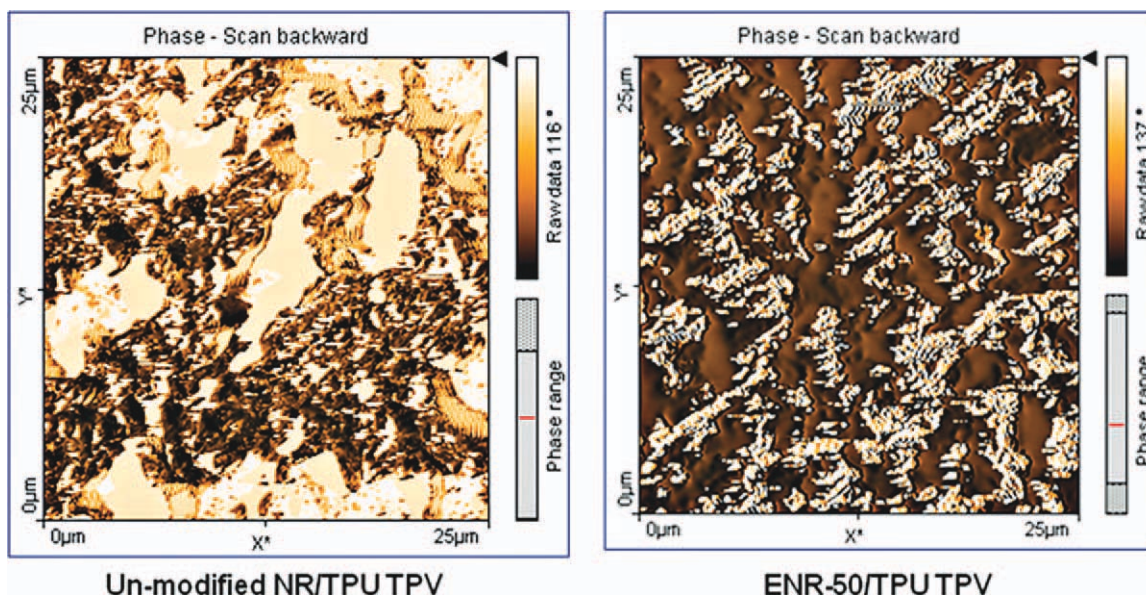


Figure 9. AFM micrographs of NR/TPU TPVs with unmodified NR (left) and ENR-50 (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PP TPV, the mechanical and thermal properties of the TPV prepared in our laboratory gave slightly lower values. However, we had to consider that the Shore A hardness of the EPDM/PP grade was also slightly higher (~ 74), and therefore, the results were not directly comparable. Most important was the improved oil resistance of the material. Even at a temperature of 150°C , the swelling in engine oil was only 12% for the optimized TPV developed in this work. This was much lower than with a typical TPV (EPDM/PP) and was also lower than a commercial-grade ETPV. This indicated excellent oil-resistance properties in the material. Furthermore, the compression set at 100°C of the TPV based on ENR/TPU was comparable to or even better than commercial grades. Also, the TSSR index (RI), a similarity index for a material's compliance compared to the behavior of ideal elastomers, made clear that the properties of the ENR/TPU-based TPV were equivalent to other typical TPVs. In summary, the optimized TPV based on ENR/TPU exhibited promising overall properties, in particular, high oil and heat resistances.

CONCLUSIONS

NR and TPU blends were prepared with a dynamic vulcanization technique. The effects of the sulfur curing systems, accelerator types, optimization of mixing process, and NR types on the properties of the TPVs were systematically investigated. The sulfur EV curing system provided a better tensile strength than the SEV and CV systems, respectively. This was attributed to the higher thermal stability of the rubber phase with EV, whereas the less thermally stable rubbers with SEV and CV showed strong reversion in curing properties. Hence, the EV curing system was the best among these alternatives for the extreme processing conditions of TPV. TPVs prepared with DCBS as an accelerator exhibited the highest tensile strength, and the action of the accelerators were ranked as follows: DCBS > TBBS > CBS > Mixed TBBS/TMTD and > TMTD. The tensile strength of the TPVs was related to the t_{s1} values of the rubber compounds. Mechanistically, a slower t_{s1} provided a longer effective time for melt mixing and, thus, a reduction in the particle size of the

Table VI. Final Properties of the Optimized TPV Based on the Dynamically Cured ENR/TPU Compared with Typical Commercial TPVs

Property	ENR/TPU TPV	ETPV ^a	EPDM/PP TPV ^a
100% modulus	3.5 ± 0.8	2.3 ± 0.0	3.4 ± 0.0
Tensile strength (MPa)	7.3 ± 0.3	5.7 ± 0.2	9.8 ± 0.2
Elongation at break (%)	326 ± 20	476 ± 28	590 ± 10
Hardness (Shore A)	61 ± 1	62 ± 1	74 ± 1
TSSR, T_{50}	102.0	96.1	108.4
TSSR index (RI)	0.59	0.62	0.63
Compression set (%; 100°C , 24 h)	50.5 ± 3	53.8 ± 2	44.4 ± 4
Swelling in ASTM oil no. 1 (%; 23°C , 70 h)	6.2 ± 1.4	—	—
Swelling in engine oil (%; 150°C , 24 h)	11.7 ± 0.1	13.0 ± 0.1	40.5 ± 0.5

^aCommercial grade with different hardnesses (~ 74 , Shore A).

rubber phase in the TPU matrix. Near optimal mixing parameters were a rotor speed of 100 rpm at about 190°C for 6 min in terms of the overall properties of the dynamically cured NR/TPU blend. ENR performed better than unmodified NR in the dynamically cured blends with TPU. Increasing the epoxide content in ENR improved the properties of the blends; this may have resulted from stronger polar interactions and possibly even the chemical bonding of ENR and TPU at the interface of the phases. The latter hypothesis will be the subject of our further investigations. As a result, a further reduction in the size of the rubber particles was observed with increasing epoxide content. The overall final mechanical and thermal properties of the TPV prepared under near optimal conditions were better than those of typical TPVs of similar hardness. Furthermore, our TPVs had outstanding oil resistance and good elastic properties. Consequently, this type of TPV exhibited useful material properties. This might lead, particularly, to industrial applications where heat and oil resistance are desired of TPVs.

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