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Research article

Influence of epoxide content and blend ratios on strength and damping properties of thermoplastic vulcanizates based on epoxidized natural rubber and poly(ether-block-amide) copolymer blends

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Abstract. Epoxidized natural rubber (ENR) with varying levels of epoxide groups ranging from 10 to 50 mol% was prepared and dynamically phenolic vulcanized by blending it with poly(ether-block-amide) copolymer (PEBA). The results indicate that the thermoplastic vulcanizates (TPVs) of ENR/PEBA blends display a sea-island morphology and enhance a number of properties. Specifically, increasing the epoxide content and PEBA proportion enhances strength properties, including higher Young's modulus (stiffness), toughness, tensile properties, and hardness, along with smaller vulcanized ENR domains dispersed in the PEBA matrix. Moreover, the decrease in tension set values indicates an improvement in the elastic properties. The attributed cause of this is the interaction between the polar groups present in the phenolic-cured ENR domains and the PEBA molecules. As a result, interfacial adhesion between the ENR domains and PEBA interfaces improved, contributing to the observed enhancements in the strength and elastic properties of the TPVs with smaller ENR domains. Furthermore, an increase in the epoxide content was found to be correlated with a decrease in tan δ and tension set, which further supported the observed improvements in strength and elasticity. Additionally, the ENR/PEBA blends showed a single glass transition temperature (T_g), while pure PEBA exhibited two T_gs. The presence of a single T_g in the ENR/PEBA blend is attributed to the overlapping of the T_g of the ENR and PEBA immiscible blend components.

Keywords: *polymer blends and alloys, epoxidized natural rubber (ENR), poly(ether-block-amide) copolymer (PEBA), sea-island morphology, damping property*

1. Introduction

Natural rubber (NR) is a bio-based polymer that is derived from the latex sap of the H*evea Brasiliensis* tree. Due to its renewable resource origin, NR is considered a more eco-friendly alternative to synthetic rubbers made from petroleum-based feedstocks [1, 2]. NR possesses unique mechanical properties such as strength, toughness, elasticity [3], and damping ability [4], making it suitable for various industrial applications. Also, its highly flexible polymer chains enable NR to stretch and recoil easily, providing excellent elasticity and resilience. Therefore, NR finds applications in products such as tires, hoses, balls, cushions, and gloves [5]. In addition to its elasticity, NR also exhibits excellent damping properties or damping factors, which means it can absorb and dissipate mechanical energy in the form of heat during vibration or oscillation. This is because NR has low internal friction due to the interaction between its polymer chains, which allows it to convert mechanical energy into heat [6]. This property makes NR particularly useful

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in applications where vibration damping is important, such as in suspension systems for vehicles or in the construction of buildings and bridges along with shock absorbers (anti-vibration) [7]. While NR has several advantages, it also has some limitations due to its highly unsaturated polymeric backbone. This results in poor resistance to heat, oil, oxygen, and ozone, which can limit its use in certain industrial applications [5]. To overcome these limitations, chemical modifications of the NR molecules have been explored to develop NR derivatives with improved properties and a better balance of characteristics [8]. Epoxidized natural rubber (ENR) is a favored candidate for addressing the limitations of NR because it has a high polarity that provides excellent resistance to oils and non-polar solvents, as well as high impermeability to gases and oils [9]. ENR is also compatible with polar polymers and fillers while retaining the unique mechanical properties of NR, including strength and toughness due to strain-induced crystallization and elasticity, especially its damping properties [10, 11].

Polyether block amide (PEBA) copolymer, also known as Pebax®, is a semi-crystalline polymer with a multiblock structure composed of two types of segments: rigid crystalline polyamide (PA) and amorphous flexible polyether. PEBA is commonly produced through a polycondensation reaction between a carboxylic acid polyamide (such as PA6, P11, or P12) and an alcohol-terminated polyether, which can be either polytetramethylene glycol (PTMG) or polyethylene glycol (PEG) [12, 13]. PEBA exhibits superior mechanical properties, including high flexibility, impact resistance, and fatigue resistance, as well as excellent resistance against a wide range of chemical substances. Compared with common thermoplastic elastomers (TPEs), such as thermoplastic polyolefin elastomer (TPO) and thermoplastic polyurethane (TPU), PEBA exhibits a lower material density and energy loss factor, a higher moisture vapor transfer rate, biocompatibility, and a relatively wide service temperature range, especially at low temperatures [14]. While PEBA already possesses good elasticity and reasonable damping properties, these characteristics can be further improved by blending it with other polymers, such as ENR, that possess outstanding damping properties [15]. PEBA is a versatile polymer that exhibits the ability to blend with various other polymers, such as poly(amide-*co*-poly(propylene glycol)) random copolymer for CO_2/N_2 separation [16] and thermoplastic polyurethane for biomedical applications [17].

In this work, the blending of PEBA and ENR was conducted via dynamic phenolic vulcanization, using various types of ENR with different epoxide groups in their molecules and different ENR proportions in the dynamically cured ENR/PEBA blends. The phenolic-cured system was chosen for its ability to provide the ENR blend with exceptional mechanical and set properties [18]. The main objective was to identify a material that offers a good balance of mechanical properties, along with outstanding damping properties, for use in specific industrial applications. Furthermore, incorporating sustainable green polymers such as natural rubber into engineering materials is an alternative approach to creating materials that are capable of slow biodegradation at the end of their usage life.

2. Experimental

2.1. Materials

Epoxidized natural rubber was synthesized using high ammonia (HA) concentrated latex as the raw material through performic epoxidation. The HA latex was manufactured by Yala Latex Co., Ltd. (Yala, Thailand) and had a dried rubber content (DRC) of approximately 60 wt%, along with an ammonia preservative content of 0.7 wt%. Performic acid was in-situ prepared using formic acid and hydrogen peroxide from Honeywell Specialty Chemicals Seelze GmbH (Seelze, Germany). It was used to react with natural rubber molecules to form ENR with varying levels of epoxide groups. To stabilize the latex during performic epoxidation, a non-ionic surfactant called Teric N30 (Alkylphenol ethoxylate) from Huntsman Corporation Australia Pty Limited (Brooklyn, Australia) was used. Methanol from J.T. Baker Chemicals (Phillipsburg, USA) was utilized to coagulate the ENR latex after performic epoxidation. Thermoplastic vulcanizates (TPVs) were prepared through dynamic vulcanization of Epoxidized Natural Rubber (ENR) and Pebax® 3533, a poly(ether-block-amide) copolymer manufactured by Arkema (Colombes, France). Pebax® 3533 is available in pellet form, comprising 75 wt% poly(tetramethylene oxide) (PTMO) and 25 wt% aliphatic polyamide (PA12), with a melting temperature of approximately 144 °C. Hydroxymethyl (methylol) phenolic resin, HRJ-10518 is a hydroxymethyl (methylol) phenolic resin produced by reacting octylphenol with formaldehyde, and it was used as a vulcanizing agent for the dynamic vulcanization of ENR/PEBA blends. This resin was manufactured by Akrochem Corporation, (Akron, USA).

2.2. Synthesis of epoxidized natural rubber (ENR)

The synthesis of epoxidized natural rubber (ENR) followed the experimental and characterization methods previously described [19–21]. In brief, 60% DRC HA latex was added into a reactor, and distilled water was added to reduce the DRC to 20%. Next, a non-ionic surfactant, Teric N30, was added to the mixture and then continuously stirred at room temperature for 25 min. Formic acid and hydrogen peroxide were then dropwise added simultaneously into the reactor at a controlled temperature of 50 °C for about 30 min. The reaction mixture was sampled at reaction times of 0, 0:30, 1:00, 1:20, 2:10, 2:40, 4:10, 5:50, and 7:30 h. Excess methanol was added to the latex sample to coagulate it, and then the rubber coagulum was sheeted out and washed thoroughly with clean water until the pH was around 7.0. The rubber sheet was eventually dried in an oven at 60 °C. A proton nuclear magnetic resonance spectroscopy (^{1}H-NMR), Varian Unity Inova 500 MHz Spectrometer (Varian, Griesheim, Germany) was then used to characterize molecular characteristics of the rubber molecules. Finally, the epoxide content was quantified using the Equation (1) [22]:

$$\text{Epoxide contetnt}\,[\text{mol\%}] = \frac{A_{2.70}}{A_{2.70}+A_{5.10}}\cdot 100 \quad (1)$$

where $A_{2.70}$ is the area under the signal at a chemical shift of 2.70 ppm, which indicates resonance of the methine hydrogen of the epoxirane ring, $A_{5.10}$ is the area under the signal at a chemical shift of 5.10 ppm, which indicates olefin hydrogen of cis-1,4-polyisoprene.

2.3. Compounding of ENR by phenolic vulcanization

ENRs with different epoxide group contents of 10, 20, 30, 40, and 50 mol% were firstly dried in a hot air oven at 70 °C for a minimum of 3 h. The dried rubber was then compounded with various chemical ingredients according to the formulation and mixing schedule outlined in Table 1. The compounding was conducted using an internal mixer, a Brabender® Measuring Mixer, model 50EHT 3Z, Brabender GmbH & Co.KG (Duisburg, Germany), at 40 °C, a fill factor of 0.8, and a rotor speed of 60 rpm. At the end of the compounding process, the ENR compound was removed from the mixing chamber and conditioned in a closed container for at least 24 h at room temperature.

Table 1. Compounding formulation and mixing schedule for preparation of ENR compounds.

Chemicals	Quantity [phr]	Mixing time [min]
ENR	100	3
Stearic acid	1	1
ZnO	5	1
Wingstay L	1	1
Phenolic resin	9	3

2.4. Preparation of dynamically cured ENR/PEBA blends

Epoxidized natural rubber (ENR) and poly(ether-block-amide) copolymer at a 50/50 wt% ratio as blended in an internal mixer, a Brabender® Measuring Mixer, model 50EHT 3Z, Brabender GmbH & Co. KG (Duisburg, Germany), at 160 °C. Prior to blending with the ENR compound, the PEBA copolymer was dried at 80 °C for at least 3 h, cooled to room temperature, and conditioned for approximately 3 h. During dynamic vulcanization, the ENR compound was initially incorporated into the mixing chamber at a rotor speed of 60 rpm and mixed for approximately 2 min before adding the PEBA component. The mixture was then continuously mixed for an additional 10 min to achieve a total mixing time of 12 min. Real-time monitoring of mixing torque and temperature was captured during the process. The resulting ENR/PEBA TPVs were subsequently formed into a thin sheet with a thickness of 2 mm using two-roll mills and then compression molded at 160 °C under high pressure for approximately 5 min. The mold was then cooled down by a circulating water system. This work investigated the influence of epoxide contents (10, 20, 30, 40, and 50 mol%) in 50/50 ENR/PEBA TPVs. Additionally, the effect of different blend ratios was studied using ENR-30, with various ENR-30/PEBA ratios of 20/80, 30/70, 40/60, 50/50, 60/40, and 70/30.

2.5. Characterization of ENR/ PEBA TPVs

2.5.1. Mechanical properties

The tensile properties of the TPV specimens were evaluated in terms of tensile strength, modulus, and elongation at break, following the guidelines of ASTM D412. A Hounsfield universal testing machine, Hounsfield Test Equipment (Surrey, England) was used to conduct the tests at room temperature with a crosshead speed of 500±50 mm/min. The test was performed until the failure of the specimens, and three replicates were tested for each sample. Additionally, the tension set was quantified following the guidelines of ASTM D412. For this, two marks were placed precisely at the ends of the gauge length of the dumbbell-shaped specimens. The initial length between these marks was measured for each sample, and the sample was then extended to a specified elongation at 100% and held at this condition for 10 min. After that, the tension stress was released, and the sample was conditioned at room temperature for another 10 min to allow the relaxation of the TPV specimen. The tension set was then calculated using the Equation (2):

$$\text{Tension set}\,[\%] = \frac{L - L_0}{L_0}\cdot 100 \tag{2}$$

where L_0 is the initial length between the marks before extension and L is the length between the marks after the relaxation of the specimen.

The hardness of the TPV specimen was measured in accordance with ASTM 2240. The test was conducted using a Shore durometer manufactured by Toyo Seiki Seisaku-Sho, Ltd (Tokyo, Japan) and reported in a Shore A unit.

2.5.2. Dynamic properties

The viscoelastic properties of the TPV materials were evaluated using the RheoTech MDpt Moving Die Processability Tester, Tech Pro Inc (Cuyahoga Falls, USA). A frequency sweep test was conducted at 150 °C over a range of 1–25 Hz, using a fixed oscillating strain amplitude of 3%. The dynamic properties, including storage modulus (G'), loss modulus (G''), and tanδ were quantified.

2.5.3. Thermal properties

The TPV specimen was subjected to dynamic mechanical thermal analysis (DMTA) using the DMTA V Dynamic Mechanical Thermal Analyzer, Rheometric Scientific Ltd (Piscataway, USA). The analysis was conducted in dual cantilever mode, with a frequency of 1 Hz, over a temperature range of –100 to 100 °C with a heating rate of 5 °C/min with a normal strain amplitude of 20 μm. This study reports the DMTA thermograms in terms of the relationship between tan δ *versus* the temperature of the TPV specimen.

2.5.4. Morphological characterization

The morphological properties of ENR/PEBA TPVs were examined using a Quanta 400 scanning electron microscope (SEM), FEI Company (Hillsboro, USA), with a magnification of 5000×. The specimen was first cryogenically fractured in liquid nitrogen to create new surfaces and prevent any phase deformation. The PEBA phase was then preferentially extracted by immersing the fractured surface into boiling dimethyl sulfoxide (DMSO) for approximately 20 min. Subsequently, the samples were dried in a vacuum oven at 40 °C for 12 h to eliminate solvent contamination. Prior to imaging with SEM, the dried surfaces were gold-coated. The size of vulcanized rubber domains dispersed in the PEBA matrix was eventually quantified in terms of the number-average (D_n) domain diameters by the Equation (3) [23]:

$$D_\text{n} = \frac{\sum N_\text{i} D_\text{i}}{\sum N_\text{i}} \tag{3}$$

where N_i is the number of particles with diameter D_i.

3. Results and discussion

3.1. Synthesis and characterization of epoxidized natural rubber

Epoxidized natural rubber (ENR) was synthesized to gain various levels of epoxide groups (10, 20, 30, 40, and 50 mol%) based on the analyzed results from ^{1}H-NMR spectroscopy, as shown in Figure 1. It can

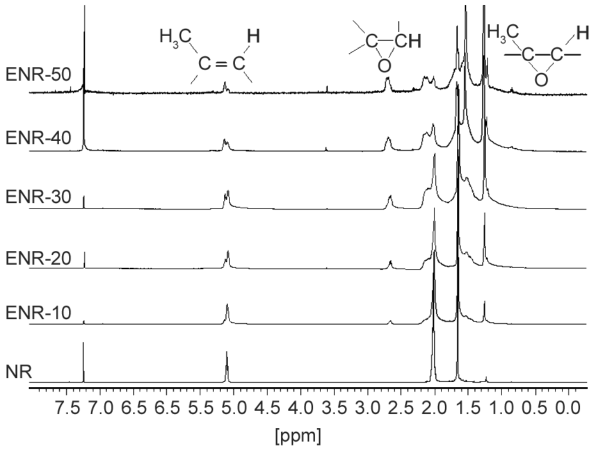


Figure 1. ^{1}H-NMR spectra of epoxidized natural rubber with varying levels of epoxide groups compared with unmodified natural rubber.

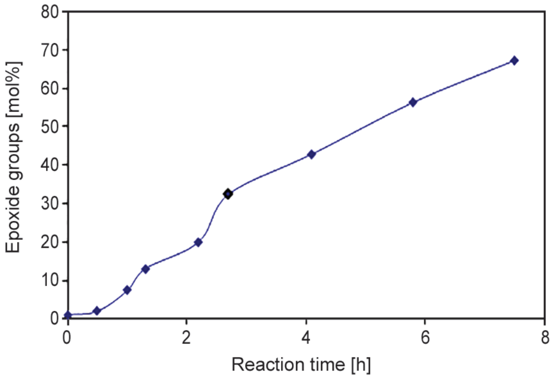


Figure 2. Relationship between reaction time and the level of epoxide groups present in ENR molecules during performic epoxidation.

be seen that the characteristic ^{1}H-NMR signals of ENR were observed at chemical shifts of 2.70, 1.20, and 3.60 ppm (for only ENR-40 and ENR-50), which correspond to the methine hydrogen of epoxide rings, methyl proton of the epoxide rings, and furan or diol proton from the opened epoxirane ring products, respectively [22, 24]. To determine the epoxidation content of the ENR samples, the area ratio of the signals at 2.70 and 5.10 ppm (indicating the olefin hydrogen of cis-1,4-polyisoprene) was calculated using Equation (1). The resulting epoxidation contents were found to be about 10, 20, 30, 40, and 50 mol%, as indicated in Figure 1. The level of epoxidation in natural rubber molecules was influenced by the epoxidation time, as illustrated in Figure 2. The relationship between reaction time and the level of epoxide groups indicates that longer reaction times lead to a higher level of epoxidation. Hence, the reaction time can be used as a parameter to determine the epoxide content in ENR molecules.

3.2. Mixing torque-time and temperature-time profiles for dynamically cured ENR/PEBA blends

Figure 3 displays the mixing torque-time and mixing temperature-time profiles of dynamically cured ENR/PEBA blends with varying levels of epoxide groups in ENR molecules (Figure 3a) and different blend proportions (Figure 3b). Initially, upon adding ENR compounds, there is a rapid decrease in mixing torque and temperature due to the softening of the rubber compound at high temperatures. In contrast, the neat PEBA component (Figure 3b) exhibits an abrupt increase in torque before rapidly decreasing within 1 min of mixing, which is attributed to the stiffness of the PEBA before melting, and the torque subsequently gradually decreases until the end of mixing. However, the torque of ENR/PEBA blends remains nearly constant until the PEBA component is added at a mixing time of around 2 min. This results in the establishment of the initial mixing range, where the mixing torque rises with an increase in epoxide content (Figure 3a) and ENR-30 content in ENR-30/PEBA blends (Figure 3b). After the addition of the PEBA component at 2 min, the mixing torque of the blends abruptly increases while the temperature declines due to the stiffness and starting temperature of PEBA. In Figure 3a, the torque subsequently decreases until the mixing time of approximately 6 min, where a gradually increasing torque is observed until the mixing time of 10 min, where the maximum torque is reached. This is attributed to the dynamic vulcanization of ENR molecules by the phenolic-cured system. The mixing torque at a given mixing time in this range also increases with

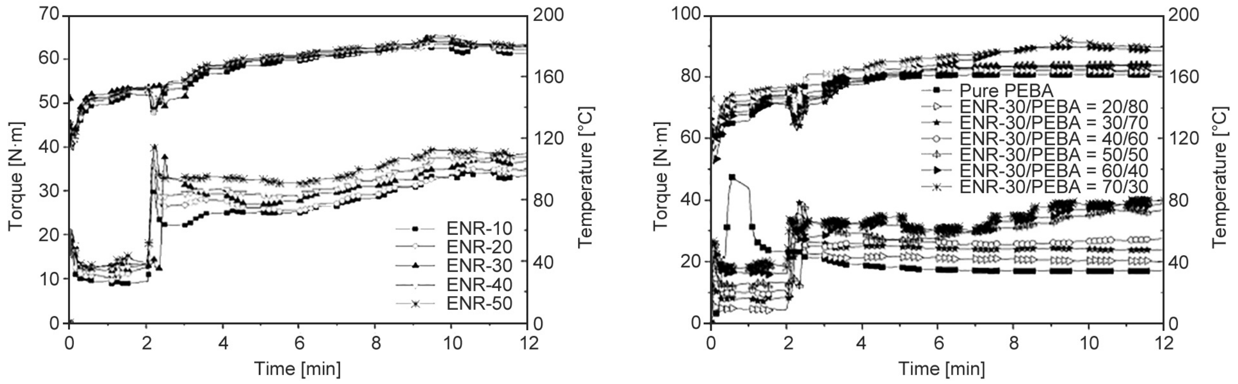


Figure 3. Mixing torque-time and mixing temperature-time profiles for dynamically cured ENR/PEBA blends. a) Blends with various levels of epoxide groups in ENR molecules. b) Blends with various ratios of ENR-30/PEBA compared to pure PEBA.

increasing levels of epoxide groups in ENR molecules. On the other hand, in Figure 3b, after a mixing time of 5 min, only ENR-30/PEBA blends with an ENR content higher than 40 wt% (*i.e.*, ENR-30/PEBA = 50/50, 60/40, and 70/30) exhibit a highly increasing trend of mixing torque. This is due to a higher degree of vulcanization and self-crosslinking of ENR molecules [25, 26], together with a higher chemical interaction between the ENR and PEBA phases. However, ENR-30/PEBA blends with an ENR content lower than 40 wt% exhibit only marginal increases in mixing torque until the end of mixing. The reason for the increased torque is due to the chemical interaction between the vulcanizing ENR and the PEBA phases, as proposed reaction mechanisms described in Figure 4. It is seen that the crosslinking of ENR with phenolic resin takes place first (reaction 1), followed by the capability of the vulcanizing ENR networks to interact with PEBA molecules via chemical interaction through their polar functional groups (reaction 2). Therefore, the polar groups in the phenolic cured ENR domain and PEBA can form intermolecular bonds such as hydrogen bonds, dipole-dipole interactions, and van der Waals forces.

These interactions can lead to a reduction in the size of the ENR domains in the TPV, which can improve the interfacial adhesion between the two phases. After a mixing time of 10 min, the mixing torque remains almost constant until the end of dynamic vulcanization at the final mixing time of 12 min due to the completion of the dynamic vulcanization and chemical reaction between ENR molecules and between the ENR and PEBA phases. It is evident in Figure 3 that the final mixing torque and temperature increased as the epoxide content in ENR molecules (Figure 3a) and the proportion of ENR-30 increased (Figure 3b). This can be attributed to the increased interaction between the polar functional groups in phenolic-cured ENR and the polar groups in the PEBA, as described in reaction (2) in Figure 4. Furthermore, a higher content of epoxide groups and a higher proportion of ENR phase in ENR/PEBA blends resulted in a higher degree of chemical interaction between the two components. This leads to a higher shearing force required to mix the ENR/PEBA blends (at a fixed rotor speed) during dynamic vulcanization and, thus, higher shear heating, which raises the mixing temperature.

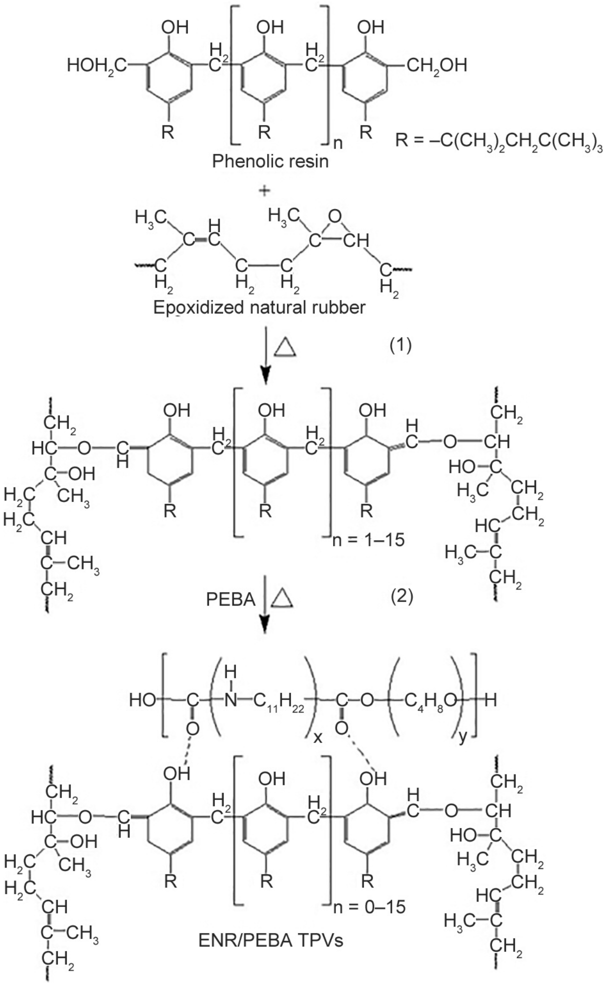
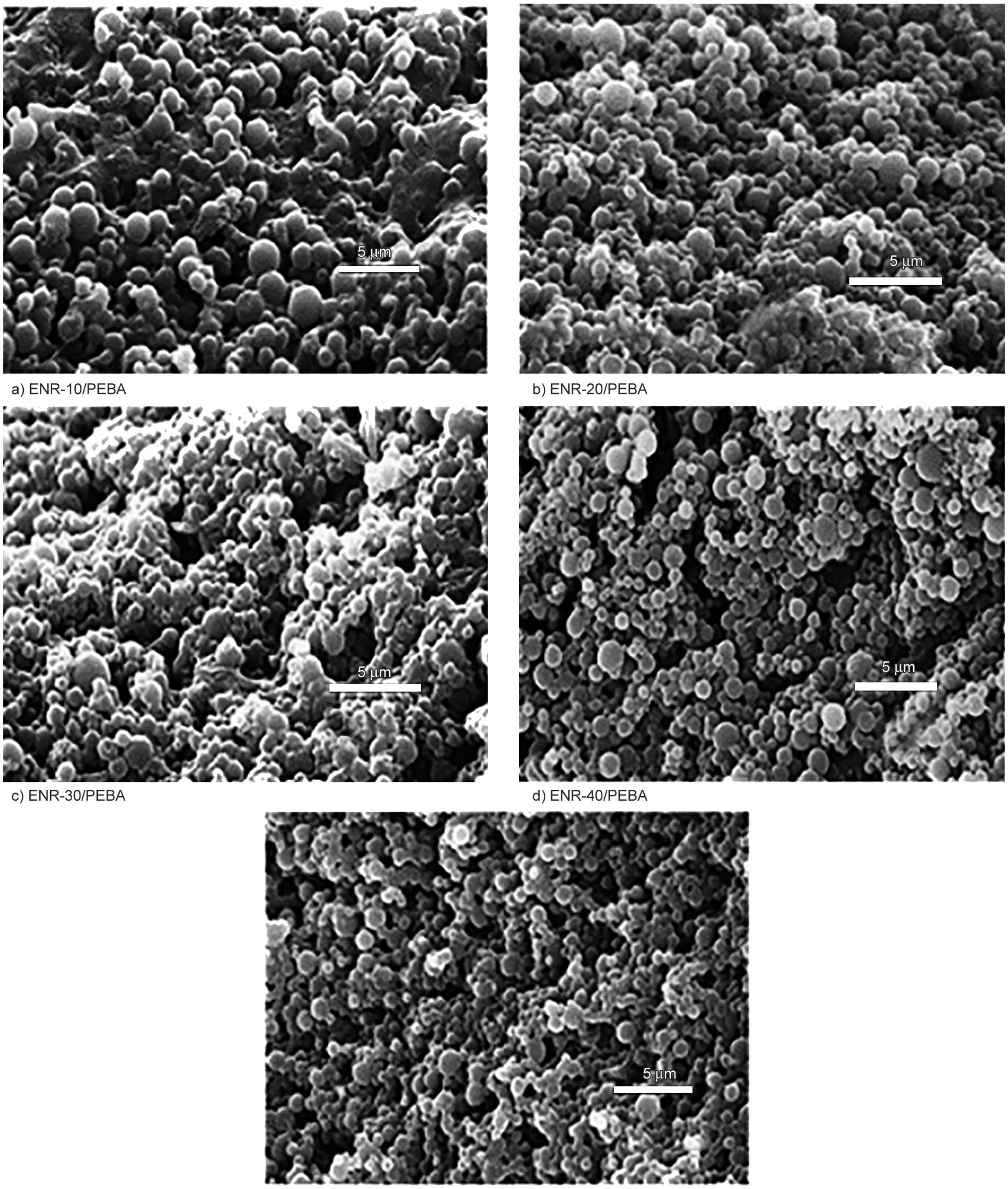


Figure 4. Proposed reaction mechanisms for dynamic vulcanization of ENR/PEBA blends. (1) Reaction of ENR molecules with phenolic curing agent. (2) Chemical interaction between phenolic-cured ENR and PEBA molecules.

3.3. Morphological properties of ENR/PEBA TPVs

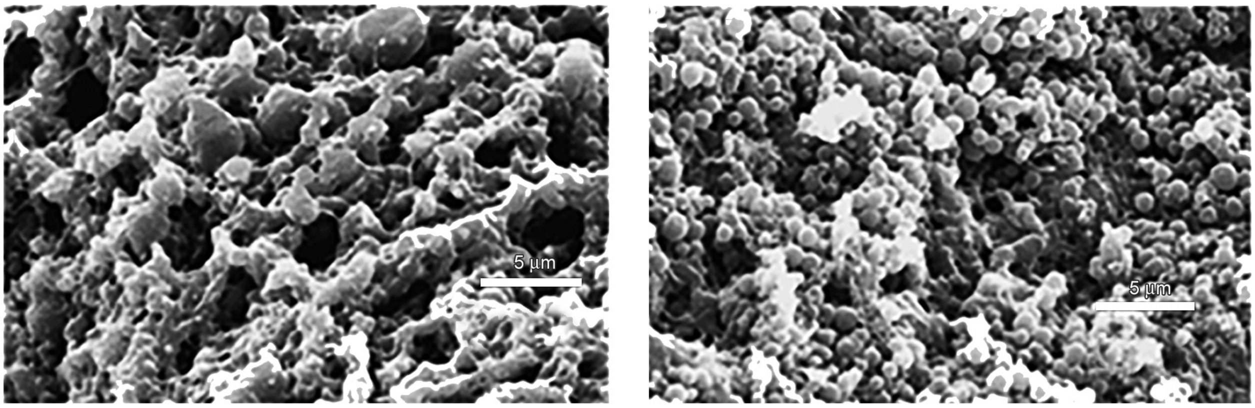
Figures 5 and 6 display SEM micrographs of dynamically cured ENR/PEBA blends with different levels of epoxide groups in ENR molecules and different blend ratios of ENR and PEBA, respectively. The micrographs clearly show the sea-island morphology of vulcanized ENR domains dispersed in the continuous PEBA matrix. Notably, the PEBA phase was preferentially dissolved by dimethyl sulfoxide (DMSO) extraction of the fractured surface of the ENR/PEBA TPV specimens. Therefore, only the spherical ENR domains are seen to adhere at the TPV surfaces. In Figure 6, large clusters of rubber domains are clearly visible in TPVs with ENR and PEBA-rich phases (*i.e.*, ENR-30/PEBA = 20/80 and 70/30, respectively). However, In Figure 5, in the blend with a fixed



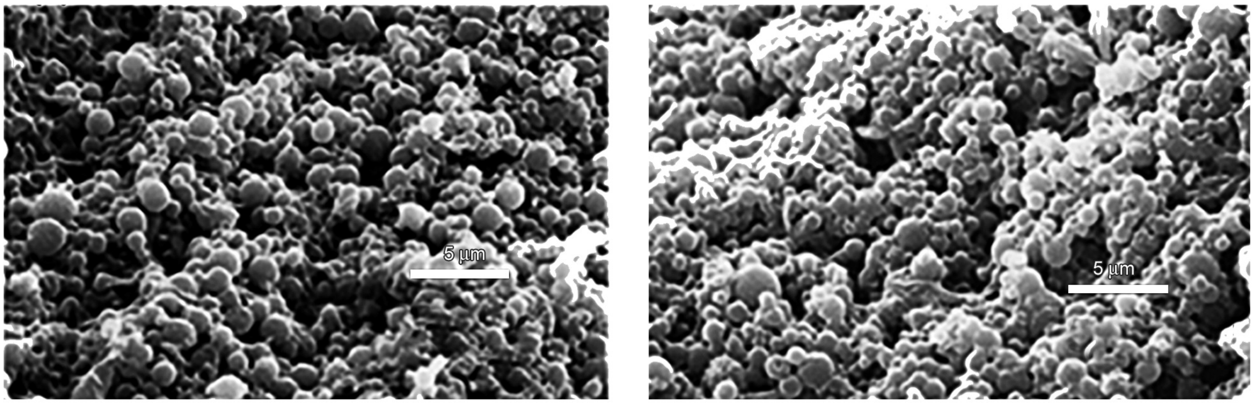
a) ENR-10/PEBA
b) ENR-20/PEBA
c) ENR-30/PEBA
d) ENR-40/PEBA
e) ENR-50/PEBA

Figure 5. SEM micrographs of dynamically cured 50/50 ENR/PEBA blends with different levels of epoxide groups in ENR molecules. a) ENR-10/PEBA, b) ENR-20/PEBA, c) ENR-30/PEBA, d) ENR-40/PEBA, e) ENR-50/PEBA.

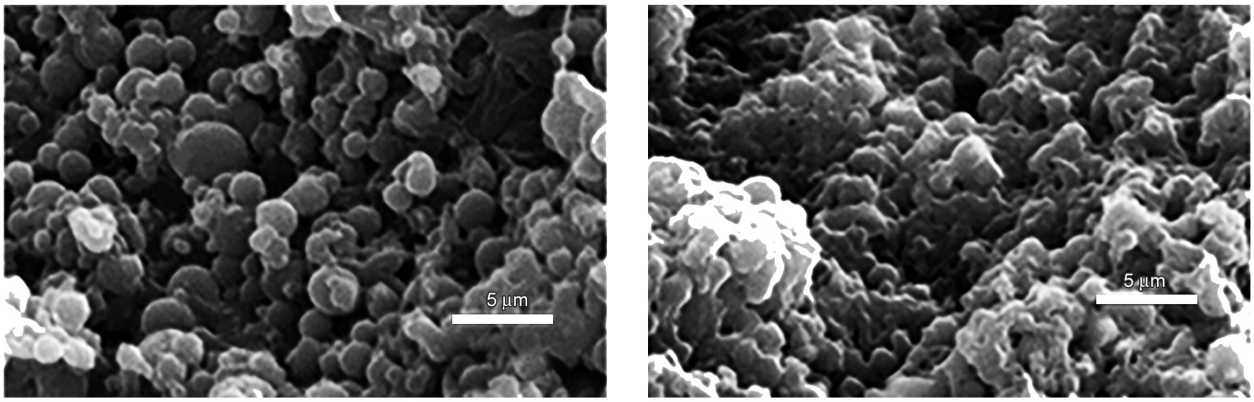
blend ratio ENR/PEBA = 50/50, it can be observed that the size of spherical ENR domains decreased as the level of epoxide groups in the ENR molecules increased. This is also clearly evident from the number-average (D_n) domain diameters of dynamically cured ENR/PEBA blends, which are shown in Table 2. This phenomenon can be attributed to the presence of a phenolic vulcanizing ENR phase (as shown in Figure 4), which results in an increase in shear viscosity during blending. This caused the blend morphology to transform from a co-continuous structure to a dispersed morphology with a severely broken down of the ENR phase into micron-scale vulcanized domains [27]. As a result, an



a) ENR-30/PEBA = 20/80 b) ENR-30/PEBA = 30/70



c) ENR-30/PEBA = 40/60 d) ENR-30/PEBA = 50/50



e) ENR-30/PEBA = 60/40 f) ENR-30/PEBA = 70/30

Figure 6. SEM micrographs of dynamically cured ENR/PEBA blends with different ENR-30/PEBA blend ratios. a) ENR-30/PEBA = 20/80, b) ENR-30/PEBA = 30/70, c) ENR-30/PEBA = 40/60, d) ENR-30/PEBA = 50/50, e) ENR-30/PEBA = 60/40, f) ENR-30/PEBA = 70/30.

increase in epoxide content leads to increased mixing torque and shear viscosity during mixing, causing the vulcanizing ENR phase to break down into smaller domains dispersed in the PEBA matrix.

In Figure 6, clear spherical rubber domains are visible in the blends with ENR/PEBA ratios ranging from 30/70 to 60/40 (*i.e.*, Figure 6b to 6e). However, for the blend with one rich phase, large clusters of rubber domains are visible in Figures 6a and 6f. This can be attributed to the influence of the viscosity ratio between the blend components, which leads to a phase inversion from a co-continuous phase to a sea-island morphology via a lamellar mechanism [28]. Therefore, the smaller average size of rubber domains (about 0.7 µm) is seen in ENR-30/PEBA blends with blend ratios ranging from 30/70 to 50/50 (Figure 6b to 6d) and Table 2). However, in the 60/40 ENR/PEBA blend, larger rubber domains at about 1.7 µm are visible (Figure 6e and Table 2), indicating an imbalance of blend proportion (or viscosity ratio)

Table 2. Number-average (D_n) domain diameters of vulcanized ENR domains in dynamically cured ENR/PEBA blends with different levels of epoxide groups in ENR molecules and different ENR-30/PEBA blend ratios.

Epoxide level [mol%]	ENR-30/PEBA blend ratio	Average particle size [µm]
10	–	1.2±0.3
20	–	0.8±0.1
30	–	0.7±0.2
40	–	0.6±0.3
50	–	0.5±0.2
–	20/80	*
–	30/70	0.7 ± 0.2
–	40/60	0.8 ± 0.1
–	50/50	0.7 ± 0.2
–	60/40	1.7 ± 0.1
–	70/30	*

where increased ENR content to 70/30 results in larger and coalescent domains forming large clusters of ENR domains (Figure 6f).

3.4. Mechanical and dynamic properties

Figure 7 illustrates the stress-strain behaviors of dynamically cured ENR/PEBA blends, which exhibit a combination of thermoplastic and elastomeric characteristics. Moreover, in Figure 7a, an increase in the level of epoxide group in ENR molecules leads to an increase in both Young's modulus (determined from the slope of the initial straight line of the stress-strain curve) and toughness (estimated from the area under the curve). This can be attributed to the enhanced interaction between polar functional groups at the interface of the vulcanized ENR domains and PEBA components (Figure 4). However, Figure 7b demonstrates a decrease in Young's modulus as the ENR proportion in the ENR/PEBA blend is increased. This is because Young's modulus is a measure of a material's resistance to deformation under an applied force. It is worth noting that increasing the amount of the elastomeric component (ENR) decreases this resistance or ability to resist deformation.

Table 3 summarizes the mechanical properties of dynamically cured ENR/PEBA blends with varying levels of epoxide groups and blend ratios, including tensile strength, elongation at break, hardness, and tension set. The relationship between stiffness, as determined by Young's modulus, and toughness, as measured by the area under the stress-strain curve, with the tensile strength, elongation at break, and hardness of 50/50 ENR/PEBA TPVs is apparent. Specifically, these properties increase with higher epoxide contents in ENR molecules. The observed phenomenon can be explained by the enhanced interaction between the two phases (Figure 4), which results in a reduction in the size of the spherical vulcanized ENR domains (Figure 5) and an increase in interfacial areas. This, in turn, leads to an improvement in interfacial adhesion between the ENR and PEBA phases. However, as the proportion of ENR-30 in the ENR-30/PEBA blends increases, the tensile strength, elongation at break, and hardness decrease due to the reduced thermoplastic component content, resulting in a reduction in strength and hardness properties. In contrast, it is generally expected that the elongation of the blends will increase as the rubber component content increases. The opposite trend observed in this case suggests the presence of other contributing factors that require further investigation. However, as shown in Table 3, blending PEBA with ENR offers the advantage of reducing hardness and creating a softer material with lower set properties (*i.e.*, high elasticity). Notably, thermoplastic vulcanizates (TPVs) that exhibit low tension sets indicate

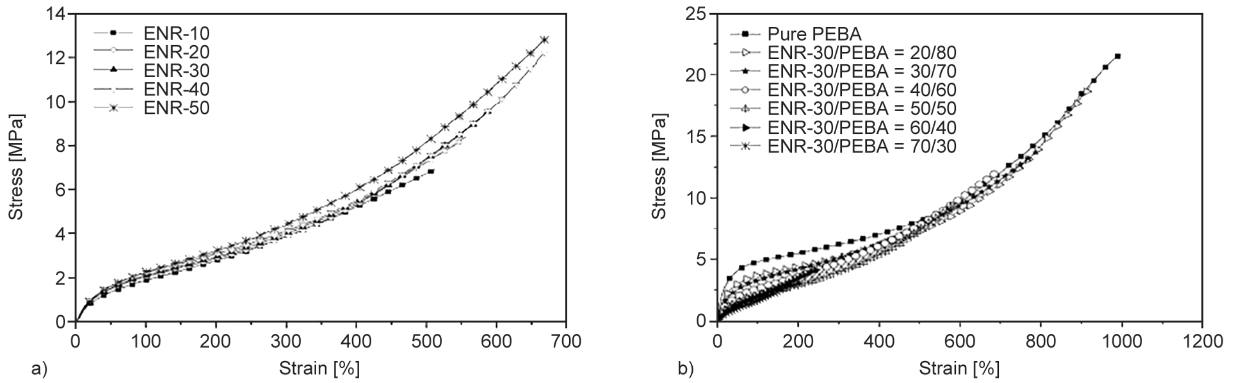


Figure 7. Stress-strain curves for dynamically cured ENR/PEBA blends. a) Blends with different levels of epoxide groups in ENR molecules. b) Blends with different ENR-30/PEBA blend ratios compared to pure PEBA.

Table 3. Mechanical properties of dynamically cured ENR/PEBA blends in terms of tensile strength, elongation at break, hardness, and tension set with different levels of epoxide groups in ENR molecules and ENR-30/PEBA blend ratios.

Epoxide level [mol%]	ENR content [wt%]	Tensile strength [MPa]	Elongation at break [%]	Hardness [Shore A]	Tension set [%]
10	–	6.8±0.2	462±30	55.5±0.5	6.1±0.4
20	–	8.4±0.3	556±25	57.5±0.5	6.0±0.5
30	–	9.6±0.4	593±14	63.5±0.6	5.8±0.3
40	–	12.3±0.3	669±26	64.5±0.5	5.8±0.6
50	–	12.9±0.1	673±04	65.0±0.9	5.6±0.5
–	Pure PEBA	21.6±0.3	999±28	77.0±0.6	13.8±0.3
–	20	19.1±0.1	923±16	75.0±0.5	11.0±0.3
–	30	13.7±0.4	789±10	72.0±0.3	10.3±0.2
–	40	12.3±0.2	685±25	68.0±0.8	9.3±0.1
–	50	9.6±0.4	593±14	64.0±0.6	5.8±0.3
–	60	4.2±0.1	248±14	55.0±0.8	5.0±0.1
–	70	3.1±0.1	203±29	44.0±1.0	4.6±0.3

superior elastic recovery properties, enabling the material to regain its original shape after being stretched. On the other hand, high tension set suggests that the material may undergo permanent deformation and may not recover its original shape. For applications where repeated deformation and recovery cycles are needed, such as in gaskets or seals, a material with a low tension set is preferred as it can maintain its functional properties over time.

As shown in Table 3, the ENR/PEBA TPVs exhibit lower tension set than pure PEBA, and the set decreases as the epoxide and ENR contents increase. This trend is consistent with the behavior of the loss tangent (tan δ), as illustrated in Figure 8. This clearly indicates that the loss tangent decreases as the epoxide group and ENR proportion increase in the TPVs (Figures 8a and 9b, respectively). It is worth noting that the loss tangent (tan δ) is a measure of a material's energy dissipation properties under cyclic deformation. The loss tangent is associated with the material's damping properties and its capacity to absorb and dissipate energy when subjected to cyclic loading. Thus, a lower tan δ value in TPVs indicates that the material has reduced energy dissipation properties and is more elastic in nature. This property can be advantageous in applications where high elasticity is essential, such as in seals, gaskets, and other engineering elastomeric articles.

Figure 9 illustrates the storage modulus of dynamically cured ENR/PEBA blends as a function of oscillating frequency, with varying levels of epoxide groups in ENR molecules and blend ratios. The results show a clear correlation between the storage moduli of TPVs with different epoxide contents (Figure 9a) and blend ratios (Figure 9b), as determined from dynamic testing with a fixed oscillating strain amplitude of 3% at 150 °C, and other mechanical properties such as Young's modulus (Figure 7), tensile strength, and hardness (Table 3). This suggests that the interaction between the ENR and PEBA phases remains. However, it should be noted that under dynamic testing conditions at 150 °C, the properties of both ENR and PEBA may be affected, and the interaction between them could potentially

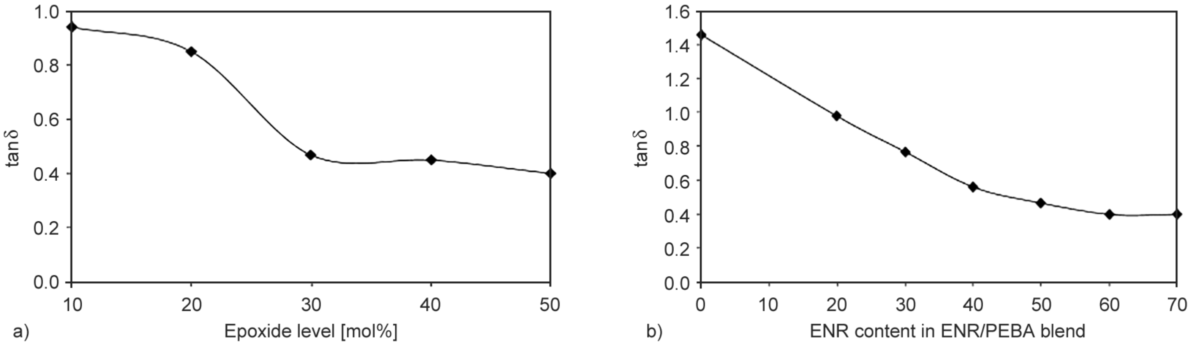


Figure 8. Tan δ *versus* epoxide level (a) and tan δ *versus* epoxide content (proportion) (b) in dynamically cured ENR/PEBA blends at a fixed oscillating frequency of 25 Hz, strain amplitude of 3% at 150 °C.

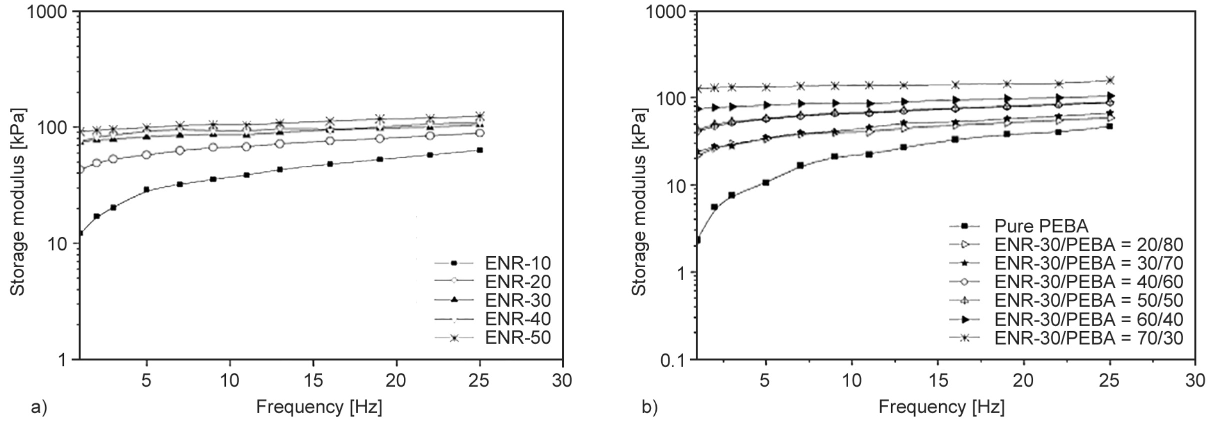


Figure 9. Storage modulus as a function of oscillating frequency for dynamically cured ENR/PEBA blends. a) Blends with different levels of epoxide groups in ENR molecules. b) Blends with different ENR-30/PEBA blend ratios.

change. For instance, the crosslinks in the vulcanized ENR may start to break down, or the PEBA matrix may soften or degrade. Therefore, the specific nature of the interaction between vulcanized ENR domains and the PEBA matrix under dynamic testing conditions at 150 °C would depend on various factors such as the materials' specific chemical composition and properties, the testing conditions, and the type of dynamic testing being performed. In Figure 9b, the storage modulus of pure PEBA displays different trends compared to the properties of the ENR/PEBA TPVs in Figure 7 and Table 3. This can be attributed to the fact that a material can have a high modulus in a stress-strain test performed at room temperature but a lower dynamic storage modulus at elevated temperatures. This variation in behavior can be attributed to the different testing conditions and mechanisms that control the material's response under those conditions. In a stress-strain test, the material is usually deformed at a constant rate and at room temperature. This test is commonly used to assess a material's stiffness or its resistance to deformation, and the modulus value obtained from the test is an indicator of the material's overall rigidity. On the other hand, dynamic testing is utilized to measure the viscoelastic properties of a material under oscillatory deformation at various frequencies. The dynamic storage modulus obtained from this test is an indicator of the material's ability to store elastic energy and resist deformation. At elevated temperatures, the mobility of the polymer chains increases, which can result in a lower storage modulus since the polymer chains are more flexible. Therefore, even if a material has a high modulus at room temperature in a stress-strain test, it may exhibit a lower dynamic storage modulus at 150 °C due to the increased mobility of the polymer chains.

3.5. Thermal properties

Figure 10 displays the results of dynamic mechanical thermal analysis (DMTA). Figure 10a shows the tan δ curves as a function of tested temperature for

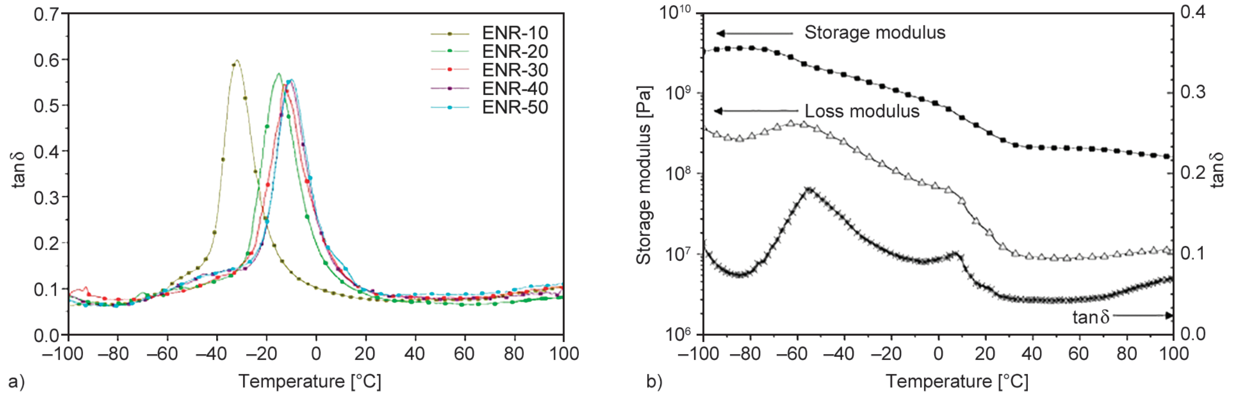


Figure 10. DMTA thermograms of ENR/PEBA TPVs with different levels of epoxide groups in ENR molecules. a) Representative tan δ curves as a function of temperature. b) Thermograms for pure PEBA in terms of storage and loss moduli, along with tan δ curves as a function of tested temperature.

dynamically cured ENR/PEBA blends with varying levels of epoxide groups in ENR molecules. On the other hand, Figure 10b presents the thermograms for pure PEBA, including the storage and loss moduli as well as tan δ curves as a function of tested temperature. It is obvious that the area under the tan δ-temperature curve of ENR/PEBA TPVs decreases as the epoxide content in ENR molecules increases (Figure 10a). This trend suggests that the material's total energy dissipation or loss factor during cyclic deformation is decreasing. It is noted that the loss factor is quantified as the ratio of the energy dissipated to the energy stored in a material during dynamic deformation. This observation is consistent with the decreasing trends of tension set in Table 3 and tan δ in Figure 8, which indicate an increasing trend of viscoelasticity in terms of elasticity for ENR/PEBA blends. These properties can serve as useful indicators of the quality and performance of the material in various applications. Furthermore, Figure 10a and Table 4 show that a single glass transition temperature (T_g) was determined from the peak of the tan δ curve, in contrast to the double T_gs observed in Figure 10b for the pure PEBA component at approximately –55 and 10 °C. The presence of a single T_g in the ENR/PEBA blends may be due to the overlapping of the T_g values of the immiscible blend components. In addition, it was observed that the T_g of the blends increased as the epoxide content in ENR molecules increased, which is contrary to the decreasing trend observed for the set and damping properties (as shown in Table 3 and Figure 8). Increasing the epoxide content in ENR molecules increases the glass transition temperature because it leads to a higher crosslink density, which restricts the mobility of the polymer chains and reduces the free volume in the material, which leads to a higher T_g.

Table 4. Glass transition temperature (T_g) of dynamically cured ENR/ PEBA blends with different levels of epoxide group in ENR.

Epoxide level [mol%]	Glass transition temperature [°C]
10	–30
20	–13
30	–11
40	–10
50	–9

4. Conclusions

Epoxidized natural rubber (ENR) with varying levels of epoxide groups incorporated into its molecular structure was *in-house* synthesized and used to prepare dynamic vulcanizates (DVs) or TPVs based on ENR/PEBA blends, with the primary objective of improving the damping properties of PEBA. The study examined two critical parameters: the effect of the epoxide group content in ENR molecules and the impact of blend ratios in ENR-30/PEBA blends on various TPV properties. The results showed that an increase in the content of epoxide groups in the range of 10 to 50 mol% and the ENR proportion in ENR/PEBA TPVs resulted in improvements in the final mixing torque, tensile strength, hardness, storage modulus, and Young's modulus. This enhancement is attributed to the improved chemical interaction between the polar functional groups in the phenolic vulcanized ENR domains and the PEBA molecules at the interface, which also led to a reduction in the size of the ENR domain dispersed in the PEBA phase of the sea-island morphology. The significant discovery of this study is that combining ENR with PEBA improved the elastic properties, particularly set properties and damping factor. Furthermore, the properties were further enhanced with higher epoxirane ring contents and increased levels of ENR proportion in the blends. Therefore, incorporating sustainable green polymers, such as natural rubber, into engineering materials like PEBA creates a possibility to develop materials with superior elasticity. This approach also offers an alternative way to create materials that can biodegrade slowly at the end of their usage life.

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