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Research Article

Effect of Epoxidized Natural Rubber as A Compatibilizer in Thermoplastic Polyurethane/Natural Rubber Blends

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Abstract: This study investigates the influence of epoxidized natural rubber (ENR) as a compatibilizer in thermoplastic polyurethane (TPU)/natural rubber (NR) blends, which were prepared through an internal mixer and compression molding. The mixing condition and mechanical properties optimization of the blends were examined following the variation of ENR concentrations. The mixing torque during blending was used to assess the homogeneity degree and processing characteristics based on the incorporation of the ENR. Mechanical properties in terms of tensile properties and impact strength were investigated to elucidate the role of ENR in enhancing the strength of the blends. The modulus and tensile strength increased by adding ENR, reaching an optimal concentration at 3 phr. Also, impact strength confirms the beneficial effects of ENR by exhibiting increased toughness and resistance to impact-induced failure at an appropriate amount of ENR to prevent aggregation when the quantity is excess. These findings highlight the ability of ENR to promote compatibility and enhancing the mechanical properties of TPU/NR blends at 3 phr of ENR loading, offering insights into the development of high-performance elastomeric materials. The presented homogeneous TPU/NR and ENR combination enables the blend for various applications, particularly filament fabrication and 3D printing product development.

Keywords: Epoxidized natural rubber, Compatibilizer, Thermoplastic polyurethane, Natural rubber, Polymer blends

1. Introduction

Three-dimensional (3D) printing technology, also known as additive manufacturing, is rapidly advancing and revolutionizing industrial production. It offers significant advantages, such as the ability to quickly fabricate complex prototypes and customize products to meet user-specific needs. With diverse printing techniques and low production costs, 3D printing enables the efficient and flexible creation of a wide range of products [1]. Among these techniques, fused deposition modelling (FDM) is widely utilized. However, FDM printers are generally limited to using a single-source filament, which restricts prints to one type of plastic. This limitation impacts the mechanical properties and functionality of printed objects due to the lack of material variety [2]. Addressing issues related to strength and durability in 3D printing technology is essential to broaden its application. Innovations in filament composition can significantly enhance the strength and durability of printed materials, enabling the use of 3D-printed objects in more extreme conditions, such as in environments involving liquids, molten substances, or high temperatures and pressures [3]. To overcome these challenges, thermoplastic elastomers (TPEs) have emerged as a promising solution. TPEs

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combine the properties of vulcanized rubbers with the ease of thermoplastic processing, making them particularly suitable for 3D printing [4].

Among the various types of TPEs, thermoplastic/rubber blends have garnered significant attention due to their cost-effective manufacturing processes and compatibility with advanced plastic processing equipment [5]. These TPEs are typically categorized into two distinct classes: thermoplastic polyolefins (TPOs) and thermoplastic vulcanizates (TPVs) [6], in which the rubber phase is unvulcanized and vulcanized, respectively. Notably, thermoplastic polyurethanes (TPUs) are considered attractive TPEs, as they consist of crystalline multi-block copolymers composed of crystalline hard segments, which provide excellent mechanical strength and amorphous soft segments, which impart good elastomeric properties. However, TPUs are often limited by relatively poor shape recovery and damping properties. These limitations can be addressed by incorporating natural rubber (NR), which enhances their suitability as soft materials for 3D printing. This is particularly advantageous for medical applications, such as prosthetic devices and soft splints, where high elasticity, comfort, and the ability to be easily customized to fit individual patient needs are essential. However, the difference in polarity between TPU and NR, due to their distinct chemical structures, affects their compatibility and, consequently, the properties of the resulting blend [7].

To enhance the interaction between TPU and NR molecules, the present work focuses on using epoxidized natural rubber (ENR) as a compatibilizer to develop dynamically cured TPU/NR blends. This approach addresses some of the inherent drawbacks of NR, such as its low polarity and its sensitivity to heat, oxygen, and ozone, due to the presence of unsaturated molecules, primarily *cis*-1,4-polyisoprene. To verify the physical and chemical interactions among TPU, NR, and ENR, mixing torque, tensile properties, impact strength, and the proposed chemical reaction are examined. It should be noted that the present TPU/NR blend does not exhibit co-continuous phase morphology, as NR concentrations higher than 10 phr result in significantly reduced hardness and render the material unsuitable for processing through the FDM technique. Therefore, the main objective of this work is to develop TPU/NR-ENR blends suitable for 3D printing applications, focusing on filament fabrication and optimizing printing conditions following the improvement of mechanical performance relative to pristine TPU/NR.

2. Methodology

2.1 Materials

Natural rubber (NR) was used as an elastomer component in TPU/NR blends. Epoxidized natural rubber with an epoxide content of 25 mol% (ENR-25), was manufactured by Muang Mai Guthrie Co., Ltd. (Surat Thani, Thailand). Thermoplastic polyurethane (TPU) is a polyether-based TPU, Elastollan grade, with a hardness of 95 Shore A was used for blending with NR and ENR. It was provided by Liack Seng Trading Co., Ltd. (Bangkok, Thailand). Mercaptobenzothiazole disulfide (MBTS) was manufactured by Monflex (Termoli, Italy). Modified zinc oxide with silicon dioxide nanoparticles ($ZnO-SiO_2$) and sulfur was provided by Global 60 Chemical Company Limited (Samut Prakan, Thailand). Stearic acid was purchased from Imperial 61 Chemical Company Limited (Pathum Thani, Thailand). Wingstay L was manufactured by Synthomer UK Ltd. (United Kingdom).

2.2 Preparation of NR compound

The preparation process of the NR composites began with the mastication of NR and ENR, which acts as a compatibilizer in various amounts of 0, 3, 5, and 10 phr for optimal 3 min until the torque reached the constant. This was performed using an internal mixer (MX500, Charoen Tut Co., Ltd., Samutprakarn, Thailand) at 60 °C under a rotor speed of 60 rpm and a fill factor of 75%. Following this, other chemicals were added according to the compounding formulation listed in Table 1. The total mixing operation lasted approximately 9 min, as outlined in the mixing process (Step 1) shown in Table 2. After mixing, the compounds were sheeted using an opened two-roll mill (Chareon Tut Co., Ltd., Samutprakarn, Thailand) and allowed to cool down to room temperature for 2 h before being blended with TPU.

Table 1 Formulation of the TPU/NR with different ENR loading

Chemicals	Amount (phr)
NR-ENR compound	
NR	100, 97, 95, and 90
ENR-25	0, 3, 5, and 10
$ZnO-SiO_2$	5
Stearic acid	1
Wingstay-L	1
MBTS	2.5
Sulfur	1
TPU/NR-ENR blends	
TPU/NR-ENR	90/10

*phr: parts per hundred rubber

Table 2 Mixing schedule the preparation of NR compound (Step 1) and dynamic vulcanization of TPU/NR-ENR blend (Step 2)

Time (min)	Mixing procedures
Step 1: NR-ENR compound	
0:00	NR and ENR-25
3:00	$ZnO-SiO_2$
4:00	Stearic acid
5:00	Wingstay-L
6:00	MBTS
7:00	Sulfur
10:00	Dump
Step 2: Dynamic vulcanization	
0:00	TPU pellets
8:00	NR-ENR compound
14:00	Dump

2.3 Preparation of dynamically cured TPU/NR-ENR blends

The preparation of TPV based on the TPU pellets and NR/ENR blend was first dried the TPU at 80 °C to eliminate moisture and then processed using an internal mixer (MX500, Charoen Tut Co., Ltd., Samutprakarn, Thailand) set to 180 °C with a rotor speed of 60 rpm. The TPU pellets were introduced into the mixer and melted for 8 min, achieving a homogeneous molten state as indicated by a stable mixing torque. Subsequently, the NR and NR/ENR were added at a TPU/NR and TPU/NR-ENR ratio of 90/10 phr. The mixing was then continued for an additional 6 min, allowing for the crosslinking of NR and NR/ENR phases within the TPU matrix, as shown in the mixing process (Step 2). The observed increase in mixing torque indicated a significant viscosity rise due to chemical crosslinking, while the stable torque confirmed the completion of the dynamically cured TPU/NR-ENR blends.

2.4 Characterization

Tensile properties

Tensile properties were determined using a dumbbell-shaped specimen prepared according to ASTM D638-14 (Type I) standard. The analysis used a universal testing machine (Zwick Z 1545, Zwick GmbH & Co. KG, Ulm, Germany). The machine operated at room temperature with a load cell capacity of 50 kN and an extension speed of 500 mm/min.

Impact strength

The samples for the Izod impact strength test were prepared with the following dimensions: a width of 64 mm, a length of 12.7 mm, and a thickness of 3.2 mm. Each sample featured a V-notch with a radius of 0.25 mm. and an angle of 45 degrees, in accordance with the ASTM D256-10 standard. The test was conducted using a pendulum with an energy of 4 J. The results were reported regarding impact strength and the type of material failure.

3. Results and discussion

Mixing torque

The mixing torque-time curves of TPU/NR-ENR blends at a 90/10 ratio with ENR loadings of 0, 3, 5, and 10 phr are depicted in Figure 1. The initial sharp peak of around 2.5 min corresponds to the introduction of unmelted TPU pellets into the mixing chamber. Subsequently, the rapid decline in mixing torque indicates the melting of crystalline TPU, while a stable torque suggests the complete melting of TPU in the continuous phase. Another peak occurs between 12-14 min, signifying increased viscosity due to incorporating NR compound. The final sharp peak before the mixing torque stabilizes indicates the degree of crosslinking among the NR molecular chains through sulfur bonding. The height of this peak reflects the physical intermolecular forces between ENR, NR, and TPU chains (TPU–ENR–NR linkages), as it influences the bulk viscosity of the TPU/NR-ENR blends. The proposed physical interaction during this mixing step is illustrated in Figure 2, showing how the epoxide rings in ENR are converted into diol functional groups under high shear forces and heat, interacting with the carbonyl groups (–C=O) in the ether soft segments and the urethane hard segments (–NH–CO–) of TPU [6]. As shown in (Figure 1), the highest mixing torque was observed when 3 phr of ENR was used, suggesting that this concentration is optimal for ENR to function as a compatibilizer between the TPU and NR chains in the blend.

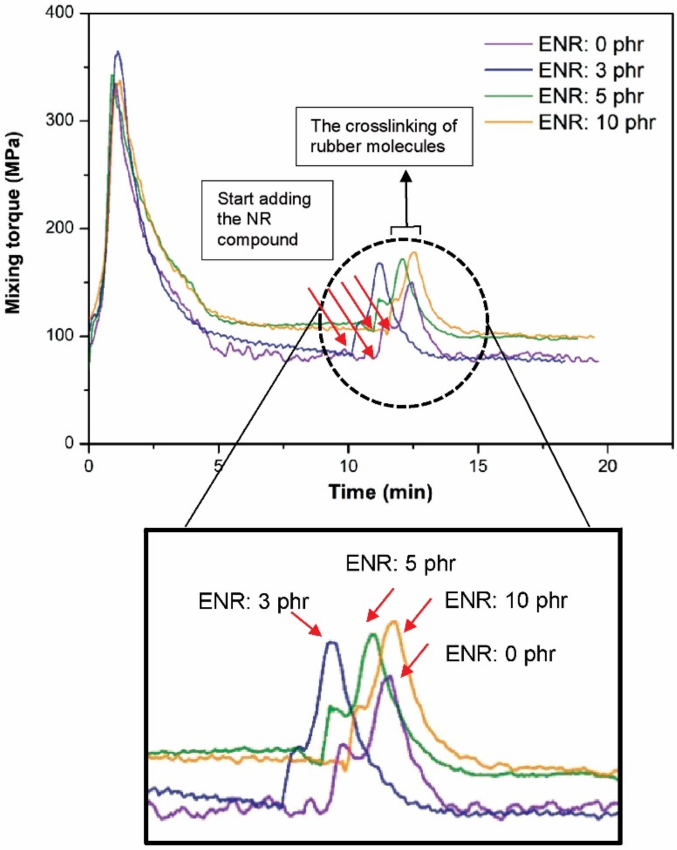

Figure 1 Mixing torque of the dynamically cured TPU/NR blends with different ENR loading.

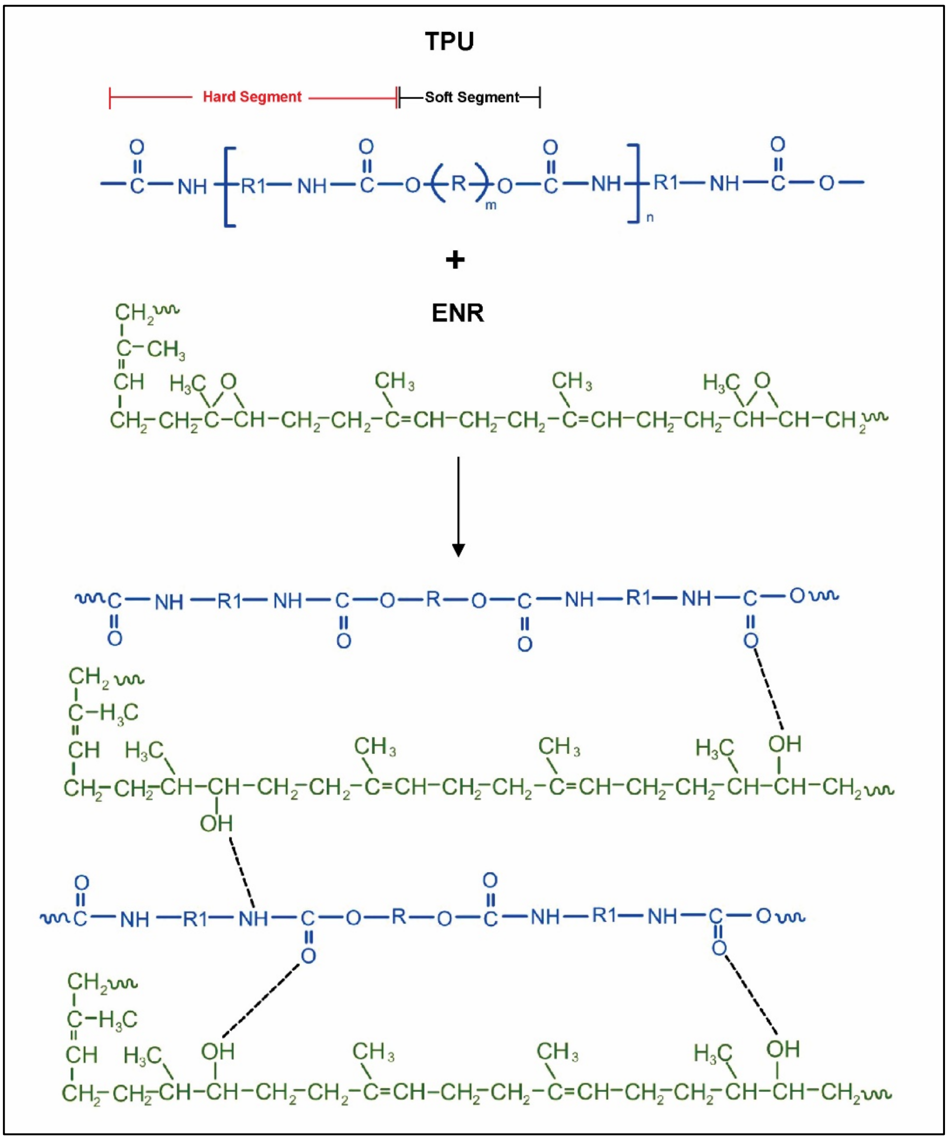

Figure 2 The scheme of chemical interaction between polar functional groups of TPU and ENR [6].

Tensile properties

The stress-strain curves of pure TPU/NR blends with varying amounts of ENR are shown in Figure 3, with the corresponding characterization summarized in Table 3. While the stress-strain curves show no yield point due to the combination of TPU and NR [8], incorporating ENR tends to increase the tensile strength and modulus of the TPU/NR blends, although the elongation at break is reduced. This is attributed to the strong interaction between the polarities of ENR and TPU. It was observed that the addition of ENR had two distinct effects on the tensile properties, as follows:

(i) At an optimal concentration, ENR acts as a compatibilizer by forming a chemical linkage between TPU, ENR, and NR, which enhances the blend's resistance to breaking under tensile forces. This was observed for the TPU/NR with 3 phr of ENR.

(ii) At higher ENR concentrations, crosslinking disruption occurs. The addition of ENR, particularly above 3 phr, results in a marked reduction in both tensile strength and elongation at break. This is because ENR may interfere with sulfur crosslinking, which also originates from the C=C bonds in the ENR chains. In addition, the higher polarity of the ENR phase reduces the interaction between TPU and NR. However, the modulus increases due to the strength of dipole and non-dipole chain interactions.

Based on the observations from (i) and (ii), the addition of ENR at 3 phr showed the most promising improvement in the TPU/NR blend properties. ENR plays a crucial role in connecting TPU and NR through the formation of polar functional groups in the polyester and polyurethane segments of TPU via dipole-dipole intermolecular forces, as well as interacting with the hydrocarbon chains of NR through dipole–induced dipole and induced dipole–induced dipole attraction forces [6]. This also explains the reduction in elongation in the TPU/NR-ENR blend compared to the blend without added ENR.

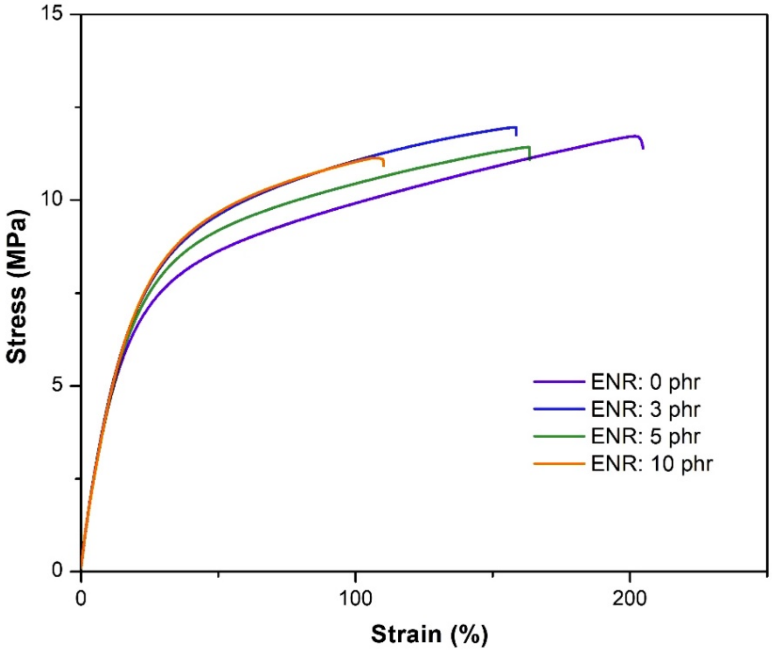

Figure 3 Stress-strain curves of dynamically cured TPU/NR blends with different ENR loading.

Table 3 Tensile properties of dynamically cured TPU/NR blends with different ENR loading

Properties	TPU/NR blend with different loadings of ENR			
	0 phr	3 phr	5 phr	10 phr
Tensile strength (MPa)	12.18 ± 0.82	12.68 ± 0.66	11.39 ± 0.24	11.19 ± 0.36
Elongation at break (%)	229.07 ± 29.01	177.00 ± 27.45	167.94 ± 4.72	111.63 ± 9.96
Young's modulus (MPa)	1.93 ± 0.16	2.00 ± 0.10	2.01 ± 0.04	2.04 ± 0.05
100% Modulus (MPa)	10.03 ± 0.72	11.22 ± 0.47	10.45 ± 0.28	11.05 ± 0.2

Impact strength

The effect of ENR loading on the impact strength of TPU/NR blends is presented in Figure 4. The sample exhibited excellent toughness without cracking during testing. As observed in the tensile properties, the addition of ENR above 3 phr reduces the impact strength of TPU/NR-ENR blends due to the self-interaction among ENR molecular chains and the excessive attraction between TPU and ENR [8, 9]. While TPU/NR and TPU/NR with 3 phr of ENR demonstrated comparable impact strength, the incorporation of 5 and 10 phr of ENR significantly reduced the strength of the blends. This suggests that the dipole–dipole interaction between TPU and ENR not only contributes to the breakage of the blend under tensile forces but also facilitates cracking in the horizontal direction. It has been reported that strong interactions among polar phases in the bulk matrix may create defect layers at the interface between polar and non-polar regions, leading to easier deformation of the blend when subjected to applied forces [10].

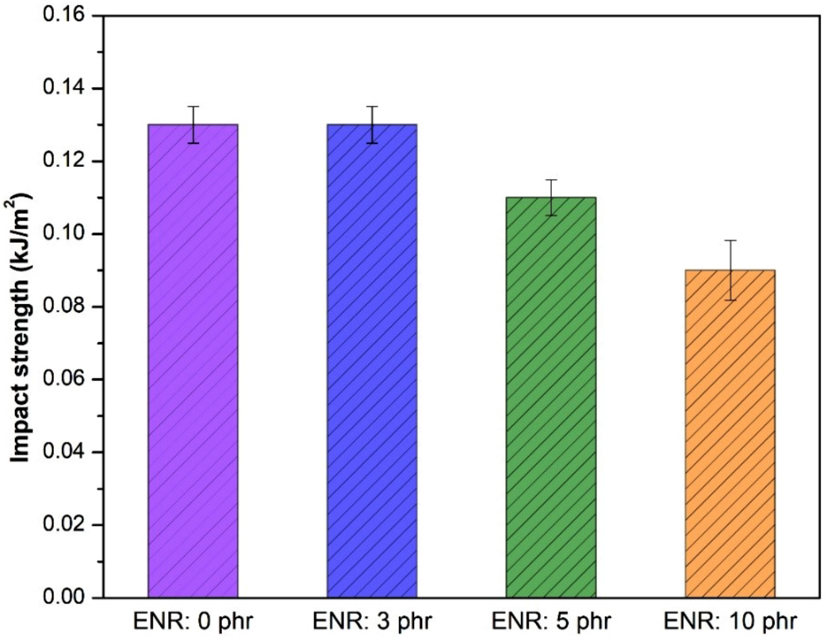

Figure 4 Izod impact strength of dynamically cured TPU/NR blends with different ENR loading.

4. Conclusion

The TPU/NR blends with ENR as a compatibilizer were developed to improve tensile and impact properties and to evaluate the effects of ENR loading within the blends. Higher mixing torque was observed due to increased shear viscosity and enhanced interactions between the polar functional groups of ENR and TPU molecules. The TPU/NR blends containing ENR exhibited excellent toughness without cracking during testing, with interactions improving up to 3 phr of ENR. Optimal tensile strength and 100% modulus were achieved at 3 phr of ENR, while the addition of ENR at 5 and 10 phr diminished the properties of the blends. This is attributed to the proper physical and chemical interactions among TPU, ENR, and NR through the dipole-dipole forces of the polar functional groups in TPU and ENR, as well as the induced dipole–induced dipole attractive forces between NR and ENR. At higher ENR concentrations, the compatibility of the TPU–ENR–NR blend was disrupted due to self-interaction among ENR chains and the formation of TPU-ENR clusters. This led to defects in the bulk matrix of the blend, reducing its resistance to breakage under both longitudinal and transverse forces. Therefore, regarding the improvement in properties, particularly strength and modulus, the viscoelastic region was enhanced, while the soft phase was reduced, providing the potential to produce filaments suitable for 3D printing applications.

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