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Strategic optimization of plasticizers, fillers, and blend ratios for enhanced performance of dynamically cured epoxidized natural rubber (ENR)/polypropylene (PP) thermoplastic vulcanizates

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Abstract

This study introduces an innovative methodology for optimizing oil, plasticizer, filler, and blend proportions in epoxidized natural rubber with 20 mol% epoxide (ENR-20) and polypropylene (PP) thermoplastic vulcanizates (TPVs), aiming to achieve superior rheological, mechanical, morphological, and thermal performance. By leveraging paraffinic oil, epoxidized soybean oil, and phthalate-based plasticizers, the research investigates their influence on tensile strength, elasticity, and processability. Among the oils and plasticizers evaluated, paraffinic oil demonstrated the most effective plasticizing performance, offering superior flexibility and elasticity. Various paraffinic oil loadings (15 phr, 25 phr, 30 phr, 35 phr, 40 phr, 45 phr, 50 phr, and 75 phr) were investigated in the 60/40 ENR-20/PP blend, with 30 phr identified as the optimum level. This formulation yielded the highest elongation at break (~410%) and a reduced tension set of less than 50%. The study also evaluates the role of carbon black and silica fillers, investigated at loadings of 10 phr, 20 phr, 30 phr, 40 phr, and 50 phr in the 60/40 ENR-20/PP blend, focusing on their reinforcement effects and contributions to thermal stability. Carbon black at 30 phr exhibited effective reinforcement, yielding tensile strength values above 7.0 MPa and elongation at break of up to 380%. Variations in ENR-20/PP blend ratios (40/60, 50/50, 60/40) demonstrate a clear pathway for optimizing phase morphology and mechanical performance. Advanced techniques such as differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) reveal critical correlations between crystallinity, glass transition behavior, and morphological features with processing parameters. These results underscore the strategic importance of tailored additive selection and precise blending methodologies, offering a roadmap to advance TPV materials for industrial applications that demand durability, flexibility, and cost-effectiveness.

1. Introduction

The study of rubber-plastic blends and their thermoplastic vulcanizates (TPVs) has emerged as a transformative focus in material science, driven by their extensive applications across diverse industries such as construction, consumer goods, medical devices, automotive, packaging, home products, aerospace, and biomedical engineering [1]. TPVs represent a cutting-edge class of hybrid materials that seamlessly combine the elasticity of rubber with the processability of thermoplastics. This unique synergy provides an exceptional balance of mechanical, dynamic, thermal, and chemical properties, positioning TPVs as essential components in modern engineering solutions [2,3]. Their versatility in delivering flexibility, durability, and cost-effectiveness makes them indispensable for a wide array of high-performance applications. TPVs are particularly valued for their remarkable thermal stability, chemical resistance, and mechanical resilience, attributes crucial for demanding environments [1]. Beyond the inherent properties of their base thermo-plastic and elastomeric components, the strategic selection and optimization of additives play a pivotal role in tailoring their performance. Additives such as fillers, antioxidants, heat stabilizers, plasticizers, and process oils are instrumental in fine-tuning properties like hardness, tensile strength, elongation, dynamic behavior, thermal stability, and elasticity. Fillers such as silica, carbon black, and calcium carbonate contribute significantly to improving mechanical strength, wear resistance, heat tolerance, and dimensional stability of TPVs [4]. Meanwhile, plasticizers and process oils are indispensable in modulating flexibility, elasticity, viscosity, and impact resistance, particularly under extreme thermal or mechanical stress [5]. These additives also enhance processability by lowering the glass transition temperature (T_g) of the polymer matrix, ensuring improved flexibility and manufacturability [6]. Furthermore, the interaction between additives and the polymer matrix critically influences the morphology and overall performance of TPVs. Proper dispersion of plasticizers can amplify elasticity while preserving structural cohesion, whereas the uniform distribution of fillers enhances stress distribution and energy absorption. Achieving an optimal balance in additive selection and dispersion is key to advancing TPV materials that excel in durability, thermal resistance, and processing efficiency. This study explores these dynamics with a focus on innovative strategies to unlock the full potential of TPVs in industrial applications.

The precise selection and optimization of oils and plasticizers are crucial for tailoring the properties of individual thermoplastic vulcanizates (TPVs), such as ethylene propylene diene monomer (EPDM)/PP-based TPVs. Studies have highlighted that paraffinic oil, a widely used process oil and plasticizer in EPDM/PP systems, plays a crucial role in enhancing phase morphology and improving processability during the dynamic vulcanization of these blends [7–11]. High paraffinic oil content accelerates the breakup of the EPDM phase during vulcanization, occurring at an earlier stage compared to blends with lower plasticizer content or without plasticizers, thereby influencing the material's final properties [7]. Recent advancements have highlighted the superior performance of ester-based plasticizers such as dioctyl sebacate, isooctyl tallate, and n-octyl oleate. These plasticizers enhance the compatibility between polymer phases, resulting in notable improvements in mechanical strength and thermal stability of TPVs [12]. Additionally, studies on flexible poly(vinyl chloride) PVC/NBR (nitrile butadiene rubber) blends have demonstrated the efficacy of using conventional plasticizers like di-2-ethylhexyl phthalate and mixtures of di-2-etylhexyl phthalate and polyester plasticizers. These formulations significantly enhance mechanical properties, oil resistance, and flexibility, underscoring the importance of synergistic plasticizer strategies in optimizing blend performance [13]. Additionally, dioctyl phthalate (DOP) has shown remarkable efficacy in reducing melt viscosity and enhancing phase compatibility in hydrogenated nitrile rubber (HNBR) and tetrafluoroethylene-ethylene-hexafluoropropylene terpolymer (EFEP) thermoplastic vulcanizates [14]. Furthermore, DOP plays a critical role in influencing the rheological properties and process variables of dynamically vulcanized PVC/ENR thermoplastic elastomers, underscoring its versatility and importance in advanced material formulations [15].

In thermoplastic elastomers derived from natural rubber, commonly referred to as thermoplastic natural rubber (TPNR), a diverse range of oils and plasticizers has been employed to enhance material performance. For example, paraffin and palm oil [16], along with paraffinic oil [17], have been utilized as plasticizers in NR/PP TPVs. Epoxidized soybean oil (ESO) has also been used to prepare oil-extended natural rubber (OENR), which is dynamically cured and blended with high-density polyethylene (HDPE) for improved material properties [18]. Additionally, paraffinic oil, treated distillate aromatic extract (TDAE) oil, and dioctyl phthalate (DOP) have been employed to optimize the properties of dynamically cured ENR/polyamide-12 (PA-12) and NR/PA-12 blends [6], as well as ENR/thermoplastic polyurethane (TPU) TPVs [19]. Moreover, the effects of low-content polycyclic aromatic hydrocarbon plasticizers, such as residual aromatic extracts (RAE) and mildly extracted solvate (MES), have been compared with natural oil plasticizers like linseed oil (LO) and rapeseed oil (RO) in NR/cellulose blends [20]. These studies highlight the strategic selection of plasticizers to tailor the mechanical, thermal, and rheological properties of TPNRs, ensuring enhanced performance across various applications.

In this study, various oils and plasticizers, including paraffinic oil (PO), epoxidized soybean oil (ESO), dioctyl phthalate (DOP), and di-iso-nonyl phthalate (DINP), were incorporated into ENR-20 compounds before dynamically curing them with PP. The selection of the optimal additive type was based on flow and mechanical property evaluations. Once the ideal additive was identified, its loading content was systematically varied to determine the optimal levels. Subsequently, two widely used fillers, carbon black and silica, were investigated at different loading levels to evaluate their impact on mechanical and thermal properties, enabling the identification of their optimal concentrations. Using these optimized filler and oil levels, the ENR-20/PP blending ratio was further optimized to achieve the best combination of material properties. The rheological, mechanical, morphological, and thermal properties of the ENR-20/PP TPVs were thoroughly investigated to determine the ideal type and loading of oil or plasticizer, as well as fillers, along with the optimal blend ratio of ENR-20/PP blends. The novelty of this work lies in the systematic optimization of TPV formulations using epoxidized natural rubber with 20 mol% epoxide (ENR-20) and polypropylene (PP), which has not been comprehensively addressed in earlier studies. ENR-20, due to its polarity, reactive epoxy groups, and compatibility with polar fillers and plasticizers, provides enhanced interfacial adhesion and elasticity. PP, a semi-crystalline thermoplastic, offers structural integrity and thermal stability. Their combination in dynamically cured TPVs enables a tunable balance of flexibility, strength, and processability, making this material system attractive for high-performance and sustainable applications. Such ENR-20/PP TPVs are particularly relevant for applications requiring flexible, durable, and reprocessable elastomeric materials, including automotive soft components, seals, vibration-damping parts, and consumer products. This multi-factorial approach advances the formulation strategies for rubber–plastic TPVs and contributes novel insights into structure–property relationships in ENR/PP-based systems.

2. Experimental

2.1 Materials

Epoxidized natural rubber with 20 mol% epoxide (ENR-20) was employed as the rubber phase, while injection-grade polypropylene (PP) served as the thermoplastic matrix in the dynamically cured ENR-20/PP thermoplastic vulcanizates (TPVs). A phenolic-modified polypropylene (Ph-PP) compatibilizer was incorporated to enhance interfacial adhesion between the rubber and plastic phases. Process oils and plasticizers included paraffinic oil (PO), epoxidized soybean oil (ESO), and phthalate-based plasticizers, namely dioctyl phthalate (DOP) and di-iso-nonyl phthalate (DINP). The sulfur-based vulcanization system for ENR-20 consisted of zinc oxide, stearic acid, TBBS, sulfur, and the antioxidant Wingstay L. For reinforcement, carbon black (N220) and silica (Ultrasil VN3 GR) were introduced, with a silane coupling agent, Bis(3-triethoxysilylpropyl) tetrasulfide (Organosilane TF800), used to promote silica dispersion and interfacial interaction. Detailed sources, synthesis procedures (including the in-house preparation of ENR-20 and Ph-PP), as well as full chemical specifications, are provided in the Supplementary Information (S1).

2.2 Influence of plasticizers

ENR-20 was initially compounded with various chemical ingredients by first being masticated on a two-roll open mill at ambient temperature, following the chemical composition and mixing steps outlined in Table 1. It is noted that ENR-20 was selected because its 20 mol% epoxidation provides an effective balance of polarity, reactivity, and flexibility, enabling good compatibility with additives, fillers, and the PP-based compatibilizer while retaining rubber-like elasticity. Lower epoxidation levels (e.g., ENR-10) offer insufficient polarity for strong interfacial adhesion, whereas higher levels (e.g., ENR-30 or ENR-50) increase stiffness and T_g, reducing flexibility and hindering proper phase breakup during dynamic vulcanization. Thus, ENR-20 represents the most suitable compromise for achieving desirable morphology and mechanical performance in ENR/PP TPVs. Different types of plasticizers, including paraffinic oil (PO), epoxidized soybean oil (ESO), dioctyl phthalate (DOP), and di-iso-nonyl phthalate (DINP), were each incorporated to investigate their influence on mechanical properties and processability. Subsequently, the ENR-20 compound underwent dynamic vulcanization in combination with PP at 160°C using a Brabender Plasticorder (Model 835205, Duisburg, Germany) equipped with tangential rotors operating at 80 rpm. The process began by softening the PP in the mixing chamber at 160°C for approximately 5 min without rotation, after which the rotor speed was set to 80 rpm for an additional 2 min to ensure complete melting. Once the PP was fully melted, the blend compatibilizer (Ph-PP) was added at a loading of 5 wt% relative to the PP content, and mixing continued for 1 min. Subsequently, the ENR-20 compound was introduced, and mixing was carried out until vulcanization was complete, as indicated by the plateau in mixing torque observed on the Brabender machine. For this study, the ENR-20/PP blend ratios were set at 60/40 and 50/50.

After mixing, the blend was removed from the mixing chamber and conditioned at room temperature for at least 3 h. The conditioned blend was then ground into small pieces using a plastic grinder machine provided by Bosco Engineering Co., Ltd. (Bangkok, Thailand). Test specimens were subsequently prepared using a specially designed mold adhering to the relevant standards, in conjunction with a plastic injection molding machine, the TII-90F model from Welltec Machinery (Cheung Sha Wan, Hong Kong). Finally, the mechanical and rheological properties of the specimens were evaluated to determine the type of plasticizer that provided optimal flow properties during processing and the optimum mechanical properties for the service life of the thermoplastic vulcanizate (TPV) materials.

After identifying the optimal type of oil or plasticizer based on superior mechanical and rheological properties, dynamically cured ENR-20/PP blends were prepared using the selected plasticizer at varying loadings of 0 phr, 15 phr, 25 phr, 30 phr, 35 phr, 40 phr, 45 phr, 50 phr, and 75 phr. The preparation process adhered to the same procedure previously described, ensuring consistency in both processing and testing conditions, in accordance with the experimental steps outlined in Figure 1.

2.3 Influence of carbon black and silica on the properties of plasticized ENR-20/PP TPVs

After determining the optimum type and loading level of the plasticizer in the previous experimental section, the influence of carbon black (N220) and silica (Ultrasil VN3 GR) was investigated. ENR-20 compounds were prepared using a slightly modified version of the mixing procedure outlined in Table 1. Initially, ENR-20 was mixed with ZnO, stearic acid, and Wingstay L, as specified in Table 1. Half of the fillers (carbon black or silica) and plasticizer were then added, and mixing was continued for 5 min. The remaining half of the fillers and plasticizer were subsequently incorporated and mixed for another 5 min. For silica, after adding the first half of the filler and plasticizer, the silane coupling agent (Bis(3-triethoxysilylpropyl) tetrasulfide) was introduced and mixed for 1 min before the second half of the filler was added. The curing accelerator (TBBS) and curing agent (sulfur) were then sequentially added and mixed as described in Table 1. Different loading levels of silica (Ultrasil VN3 GR) and carbon black (N220) at 10 phr, 20 phr, 30 phr, 40 phr, and 50 phr were investigated, alongside a control ENR-20/PP TPV without fillers. After dynamic vulcanization, the filled TPV was removed from the mixing chamber, conditioned, and ground, as described previously. Test specimens for evaluating the mechanical, rheological, morphological, and thermal properties of silica- and carbon black-filled plasticized ENR-20/PP TPVs were eventually fabricated using a TII-90F plastic injection molding machine from Welltec Machinery, (Cheung Sha Wan, Hong Kong).

2.4 Influence of blend ratios between ENR-20 and PP

Following the determination of the optimal type and loading levels of plasticizer (Section 2.2) and fillers (Section 2.3), the blend ratios of ENR-20 to PP in the filled, plasticized ENR-20/PP compounds were varied to examine their effect on the final properties of the thermoplastic vulcanizates. ENR-20 was compounded using the procedures outlined in Sections 2.2 and 2.3 before undergoing dynamic vulcanization. The blend ratios of ENR-20 to PP were adjusted to 25/75, 40/60, 50/50, 60/40, and 75/25. To improve compatibility between the rubber and thermoplastic phases, 5 wt% of a Ph-PP blend compatibilizer (based on the weight of PP) was added. Rubber compounding was carried out using the optimal type and loading level of plasticizer and filler identified in the earlier sections, along with the other ingredients listed in Table 1.

Table 1 Compounding formulation and mixing schedule for preparation of ENR-20 compounds.

Chemicals	Quantities [phr]	Mixing time [min]
ENR-20	100	5
ZnO	5.0	2
Stearic acid	2.5	2
Wingstay L	1.0	1
Oil/Plasticizers	25.0	15-20
TBBS	0.6	2
Sulphur	2.0	2

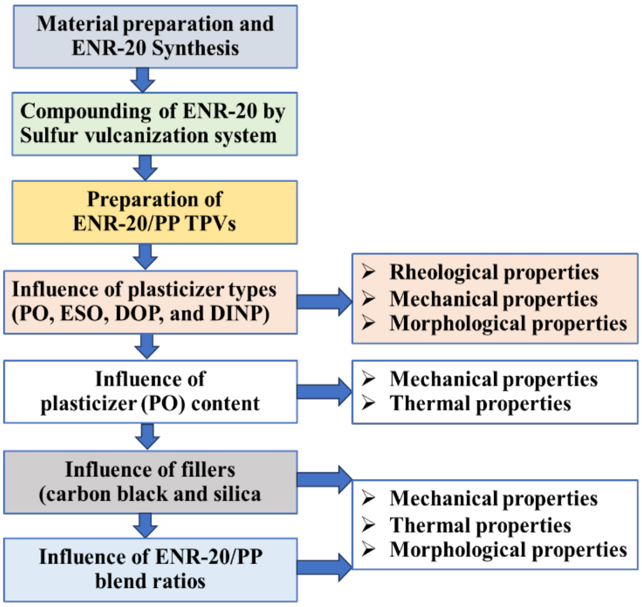

Figure 1. Flowchart illustrating the experimental steps and associated details.

The preparation of ENR-20/PP TPVs was conducted via dynamic vulcanization, wherein the ENR-20 compound was dynamically cured during melt mixing with PP. The mixing procedure, including parameters such as temperature, rotor speed (i.e., shear rate), and mixing duration, is described in Section 2.2. Following the preparation, the rheological, mechanical, thermal, and morphological properties of the TPVs were evaluated to determine the influence of blend ratios. Rheological properties were assessed to evaluate the processability and viscoelastic behavior of the ENR-20/PP TPVs. Furthermore, mechanical properties, including tensile strength, elongation at break, tension set, and hardness, were analyzed to gauge the overall performance characteristics of the blends, reflecting their suitability for various applications. Additionally, morphological studies were performed to investigate the phase distribution and microstructure of the TPVs using techniques such as scanning electron microscopy (SEM), following the experimental procedures outlined in Figure 1.

2.5 Rheological properties

The shear flow behavior of ENR-20/PP TPVs with different blend ratios was examined using a capillary rheometer, Model RH7, Rosand Precision Limited, (Stourbridge, UK). The rheometer was fitted with a flat capillary die featuring a 180° entry angle, a 2 mm diameter, and a length of 32 mm, yielding an L/D ratio of 16:1. Rheological testing was performed at 190°C across a wide shear rate range of 10 s^{-1} to 1600 s^{-1}. To conduct the tests, TPV samples were placed into the rheometer barrel, followed by the insertion of the piston, which was carefully lowered to compact the material. Excess melting material was expelled through the capillary die, and the piston was held in place for at least 5 min. This step allowed for proper compaction of the sample, full melting of the polymers, and tested pressure stabilization to baseline levels. Testing commenced once these conditions were achieved, with the piston compressing the molten material at controlled speeds corresponding to shear rates calculated by the rheometer software. As the piston descended at controlled speeds corresponding to specific shear rates, a pressure transducer measured the pressure drop across the capillary die. The data were analyzed using specialized software to calculate the apparent shear stress, shear rate, and shear viscosity, based on equations derived from the Poiseuille law for capillary flow, as described in our previous work [23].

2.6 Mechanical properties

The tensile properties of the ENR-20/PP TPVs were evaluated using a universal testing machine (Model H 10KS) from Hounsfield Test Equipment Co., Ltd., (Surrey, UK). Testing was performed according to ASTM D412 standards, using die type C. These evaluations offered valuable information about the mechanical performance of the vulcanizates, including their tensile strength and elongation characteristics under applied stress.

The tension set, also referred to as tensile set, was measured following the ASTM D412 standard. This test quantified the material's permanent deformation after elongation and relaxation, providing critical information about the elasticity and recovery properties of the vulcanizates. Dumbbell-shaped specimens were prepared using the plastic injection molding technique, with precise gauge marks placed at each end of the gauge length. The initial distance between these marks was recorded before testing. The specimens were mounted in the grips of a tensile testing machine and stretched to 100% elongation, where they were held for 10 min. After this period, the specimens were released and allowed to relax for another 10 minutes. The final distance between the gauge marks was then recorded, and the tension set was determined using the following formula [24]:

$$\text{Tension set (\%)} = \frac{\text{Final gauge length-Initial gauge length}}{\text{Initial gauge length}} \times 100 \quad (1)$$

The hardness of the TPVs was evaluated using a Shore A durometer from AFFRI Inc., (Wood Dale, USA), in compliance with ASTM D2240 standards. This test provided precise and reliable measurements of surface hardness, with the Shore A scale indicating the material's resistance to indentation. These results offered insights into the stiffness of the TPVs and their suitability for various applications. When combined with assessments of tensile strength and tension set, the hardness data contributed to a comprehensive evaluation of the mechanical performance of ENR-20/PP TPVs, supporting the optimization of their formulation and processing conditions.

2.7 Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) analysis was performed using a DSC 8500 instrument from PerkinElmer, Inc. (Shelton, USA). Temperature calibration was conducted using Indium as a reference material due to its precise and well-documented melting point and enthalpy of fusion. The sample was carefully prepared and sealed in an aluminum pan, with an empty aluminum pan serving as the reference. The analysis involved a temperature ramp from –130°C to 200°C at a heating rate of 10°C·min^{-1}. To eliminate prior thermal history and ensure consistent results, the sample was first cooled from room temperature to –130°C at the same rate. This preconditioning step ensured that thermal transitions observed during subsequent heating reflected the material's intrinsic properties. Following this, the temperature was increased from –130°C to 200°C at a heating rate of 10°C·min^{-1}, with thermal transitions continuously recorded throughout the process. The data were presented as DSC thermograms, which display enthalpy changes (heat flow) as a function of temperature. These thermograms provided key insights into the material's thermal behavior, such as the glass transition temperature (T_g) and melting temperature (T_m). The T_g was identified as a step change in the heat flow baseline, indicating a shift in heat capacity (C_p) as the polymer transitioned from a rigid, glassy state to a more flexible, rubbery state. The T_g value was determined from the midpoint of this baseline shift. In contrast, the T_m was observed as a distinct endothermic peak in the thermogram, representing the crystalline melting temperature of the polymer. The area under the melting peak corresponded to the enthalpy of fusion (ΔH_f), which quantifies the energy required to melt the crystalline regions of the material.

The degree of crystallinity (X_c) of PP was determined using the enthalpy of fusion (ΔH_f) derived from the DSC thermogram. This experimental value was compared to the theoretical enthalpy of fusion for fully crystalline PP (ΔH_f^{100}), which is 207 J·g^{-1}. The crystallinity was calculated using the following equation [25]:

$$X_{c\,(\%)} = \frac{\Delta H_f}{\Delta H_f^{100}} \times 100 \qquad (2)$$

2.8 Morphological properties.

The morphological features of dynamically cured ENR/PP blends were examined using scanning electron microscopy (SEM) with the ZEISS LEO-1450 VP instrument, supplied by Carl Zeiss AG (Jena, Germany). Test specimens of thermoplastic vulcanizates, prepared via plastic injection molding, were fractured to expose a fresh surface for analysis. To selectively remove the PP phase from the ENR/PP TPVs, the samples were treated with hot xylene for approximately 10 min. Following the solvent treatment, the specimens were dried in a vacuum oven at 50°C for about 2 h. Before SEM observation, the dried samples were coated with a thin layer of gold to enhance surface conductivity and image clarity.

3. Results and discussion

3.1 Influence of plasticizer types on the properties of ENR-20/PP TPVs

Figure 2 presents the flow curves (apparent shear stress vs. apparent shear rate) and viscosity curves (apparent shear viscosity vs. apparent shear rate) for dynamically cured ENR-20/PP blends with a 60/40 blend ratio, incorporating various types of process oils. It is evident that the blend without oil consistently exhibits the highest apparent shear stress and viscosity across all shear rates. In contrast, the addition of plasticizers (DINP, PO, DOP, and ESO) at approximately 25 phr significantly reduces both the flow and viscosity curves, indicating pronounced shear-thinning behavior. The observed reductions in shear stress and viscosity can be attributed to the role of plasticizers as internal lubricants. These additives lower intermolecular forces between polymer chains, enhance chain mobility, and increase the free volume, thereby facilitating chain movement under applied shear forces. As a result, the blends exhibit lower resistance to flow, consistent with previously reported findings on ENR/TPU thermoplastic vulcanizates (TPVs).[19] A comparison of different oils and plasticizers reveals that ESO, DINP, and DOP produce higher flow and viscosity curves compared to PO. This behavior may stem from their molecular structures, which include polar functional groups. These groups likely interact more strongly with the polar moieties in ENR molecules, resulting in increased shear stress and viscosity. Conversely, PO, with its relatively lower polarity, demonstrates weaker interactions with ENR chains, leading to reduced resistance to flow.

Another critical factor is the matching of the solubility parameters of various plasticizers with those of the parent polymers, PP and ENR. According to the literature, the solubility parameters for epoxidized soybean oil (ESO), dioctyl phthalate (DOP), diisononyl phthalate (DINP), and paraffinic oil are reported as 16.70 MPa$^{1/2}$ [26], 16.60 MPa$^{1/2}$ [27], 16.60 MPa$^{1/2}$ [28], and 16.35 MPa$^{1/2}$ [29], respectively. These values closely align with the solubility parameters of ENR (approximately 17.4 MPa$^{1/2}$ [19], and PP, around 16.76 MPa$^{1/2}$ [30].

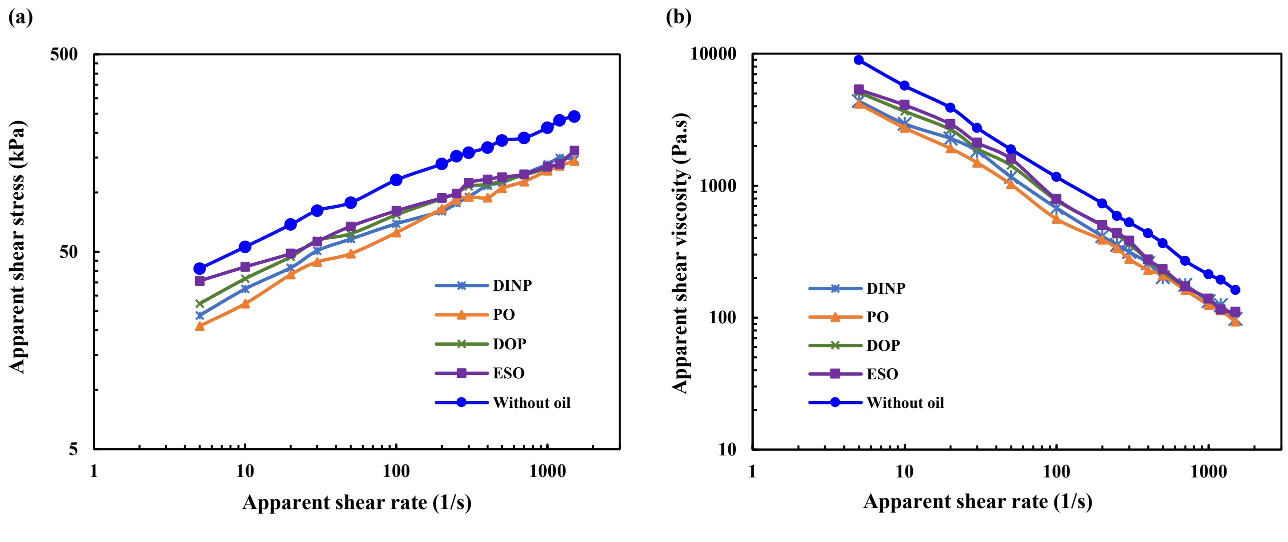

Figure 2. (a) Relationship between apparent shear stress and apparent shear rate (flow curves), and (b) relationship between apparent shear viscosity and apparent shear rate (viscosity curves) for dynamically cured ENR-20/PP blends with a 60/40 blend ratio using different types of plasticizer.

The relatively small differences in solubility parameters between PP and the additives indicate that a portion of the plasticizers in the ENR phase could diffuse into the PP phase during dynamic mixing. This diffusion likely acts as a lubricant, reducing intermolecular friction within the PP phase and subsequently lowering the overall shear stress and viscosity of the blend system. Moreover, these plasticizers significantly influence the mechanical and thermal properties of the blends, as evidenced by the results presented in Figures 3-4. The role of these additives in optimizing the microstructure and enhancing the performance characteristics of the blends underscores their critical contribution to the material's overall functionality.

Figure 3 presents the mechanical properties including tensile strength, hardness, elongation at break, and tension set of dynamically cured ENR-20/PP blends containing various types of plasticizer. These properties are analyzed for two blend ratios between ENR-20 and PP, 60/40 and 50/50. The strength-related properties, including tensile strength and hardness (Figure 3(a-b)), exhibit higher values in the 50/50 ENR-20/PP blend. This improvement is attributed to the increased proportion of the PP hard phase, which contributes to the blend's rigidity and mechanical stability. Furthermore, the 60/40 ENR-20/PP TPV demonstrates a unique microstructure, with smaller vulcanized ENR domains finely dispersed within the PP matrix. This morphology is confirmed through representative SEM images of the two blend ratios containing 25 phr of PO. The finer dispersion in the 60/40 blend enhances interfacial adhesion and interaction forces between the ENR and PP phases, leading to improved cohesion and mechanical performance compared to the coarser dispersion observed in the 50/50 blend.

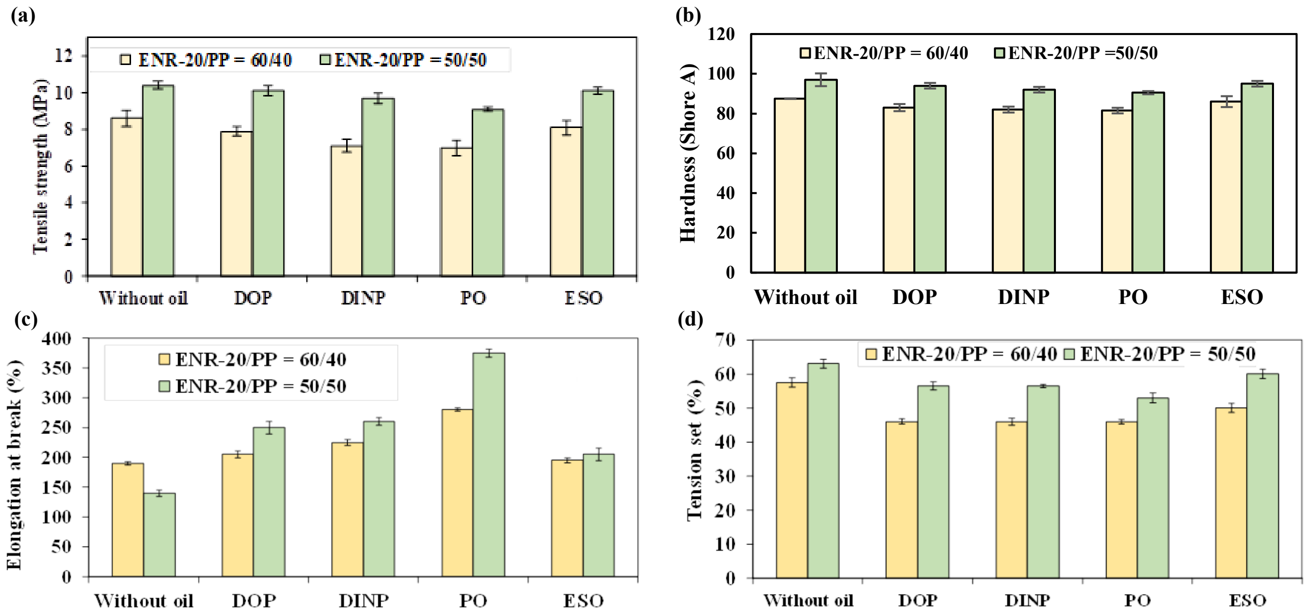

Figure 3. (a) Tensile strength, (b) hardness, (c) Elongation at break, and (d) tension set of dynamically cured ENR-20/PP blends with various types of plasticizer at blend ratios of 60/40 and 50/ 50.

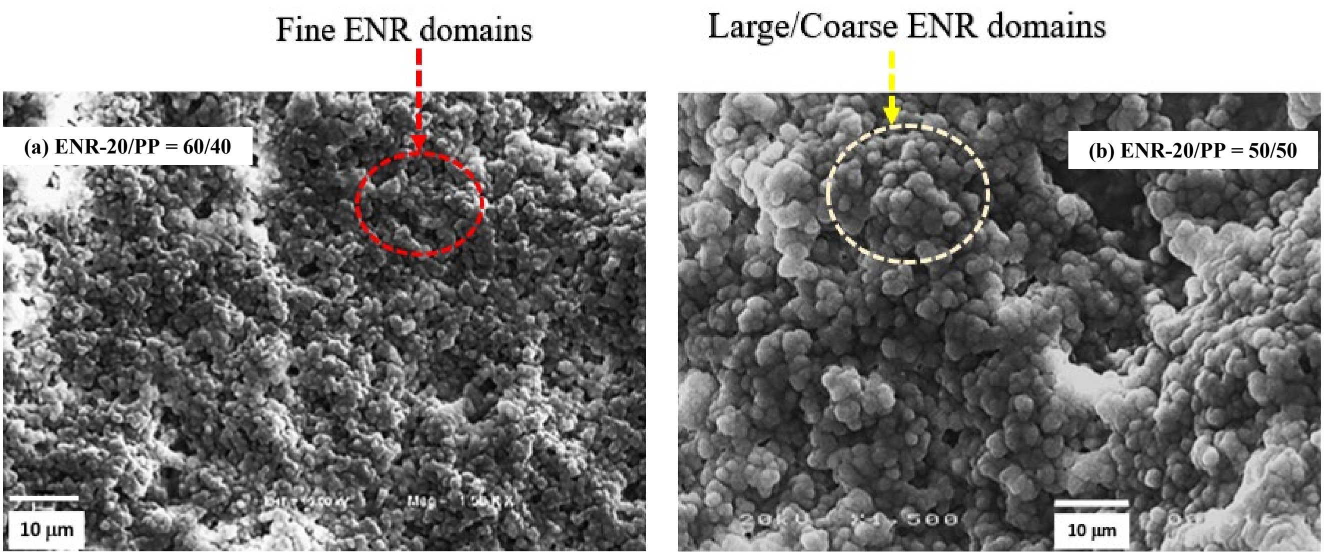

Figure 4. SEM micrographs of dynamically cured ENR-20/PP blends with PO at blend ratios of 60/40 (a), and (b) 50/50 viewed at 1500x magnification.

The tensile strength of dynamically cured ENR-20/PP blends, with and without the addition of plasticizers such as DOP, DINP, PO, and ESO, varies depending on the type of plasticizer incorporated. The inclusion of plasticizer in both the hard phase (PP) and soft phase (vulcanized ENR domains) generally leads to a reduction in tensile strength and hardness compared to blends without plasticizer. This decrease is primarily attributed to the plasticizing effect, which enhances the mobility of molecular chains and reduces the bulk density of the TPVs. However, the blends containing DOP and ESO exhibit relatively higher tensile strength and hardness compared to those with DINP and PO. This behavior may be explained by the molecular structure of ESO and DOP, where the remaining epoxy groups in ENR molecules facilitate improved phase compatibility and interfacial reinforcement. These interactions enhance the mechanical integrity of the blend. In contrast, DINP and PO, as non-reactive plasticizers with limited miscibility in the polymer phases, primarily function by softening the polymer matrix and vulcanized rubber domains. This softening effect reduces the tensile strength and hardness, as the lack of chemical interactions between these plasticizers and the polymer phases diminishes the reinforcement capability.

Figure 3(c-d) reveal that dynamically cured 60/40 ENR-20/PP blends exhibit greater elongation at break but lower tension set values compared to the 50/50 ENR-20/PP TPVs. These results highlight enhanced elastomeric properties in the 60/40 blend, attributed to the higher rubber-phase content of vulcanized ENR-20 with finer rubber domains (Figure 4). The SEM analysis confirms that the 60/40 ENR-20/PP TPV features smaller vulcanized ENR domains, estimated to be less than 1 μm in size, adhering to the surface. In contrast, the 50/50 ENR-20/PP TPV displays larger, spherical-like vulcanized ENR domains. The elastomeric properties also vary depending on the type of plasticizer used, as shown in Figure 3(c-d). The inclusion of plasticizer significantly enhances the elongation at break for all TPVs compared to those without plasticizer. Among the formulations, the TPV containing PO demonstrates the most remarkable elongation at break, reaching nearly 400%, outperforming TPVs with other plasticizers. The elongation at break follows the order: PO > DINP > DOP > ESO > without plasticizer. This trend aligns with the plasticizing effect of PO observed in other dynamically cured polymer systems, including unmodified natural rubber (air dry sheet, ADS)/PP blends [17], EPDM/PP TPVs, and polystyrene-block-poly(ethylene-co-butylene)-block-polystyrene triblock copolymer triblock copolymer (SEBS/PP triblock copolymer TPVs [31]. It is also consistent with findings in dynamically cured maleated ethylene propylene rubber (m-EPM)/PP blends [32]. Interestingly, this behavior contrasts with the plasticizing effects observed in dynamically cured ENR-25/polyamide-12 and ENR-25/TPU blends, where DOP exhibited superior tensile strength and elongation at break compared to PO. This discrepancy can be attributed to stronger chemical interactions between DOP and the dispersed ENR-25 domains, as well as the matrix phase (e.g., PA-12) [6,19]. In Figure 3(d), the TPV plasticized with PO exhibits the lowest tension set, particularly in blends with a higher ENR proportion (e.g., ENR-20/PP = 60/40). This result underscores the superior elasticity of the TPV material formulated with PO, making it an excellent candidate for applications requiring high flexibility and excellent recovery properties.

Based on the presented data, PO exhibited the lowest viscosity and most favorable flow curves (Figure 2(a-b), highlighting its superior processability. Additionally, PO demonstrated the lowest tension set (Figure 3(d)) and the highest elongation at break (Figure 3(c)), indicating exceptional rubber elasticity. These enhanced elastomeric properties were achieved without significantly compromising tensile strength and hardness, as shown in Figure 3(a-b). Given these advantages, PO was selected as the plasticizer for preparing TPVs to investigate the effects of filler types (carbon black and silica) on ENR-20/PP TPVs. This study aims to optimize the balance between material performance and processability, tailoring the properties of TPVs for industrial applications where both flexibility and durability are critical. Therefore, the mechanical trends in Figure 3 align with the morphological observations in Figure 4. The 60/40 ENR-20/PP blend exhibits smaller and more uniformly dispersed vulcanized ENR domains, which improve interfacial adhesion and stress transfer, contributing to its lower tension set and superior elastic recovery. In contrast, the 50/50 blend contains larger ENR domains, but its higher PP content provides a stronger load-bearing network, resulting in higher tensile strength and, in some cases, higher elongation at break when plasticizers are present. Therefore, the mechanical performance arises from the combined effects of domain size/morphology and blend composition, where finer morphology enhances elasticity, while higher PP fraction improves strength and extensibility.

3.2 Influence of PO content on the properties of ENR-20/PP TPVs

Figure 5 depicts the tensile strength, hardness, elongation at break, and tension set of dynamically cured 60/40 ENR-20/PP blends with varying PO loadings. The addition of PO causes a gradual decrease in tensile strength and hardness (Figure 5(a)), which can be explained by several key factors. Firstly, the compatibility of the solubility parameters between PO and the PP phase enables the oil to diffuse into the PP matrix, altering its morphology and resulting in a softer and less rigid structure. Secondly, as an effective plasticizer, PO reduces intermolecular forces within both the PP matrix and the dispersed ENR rubber domains, increasing molecular mobility and softening the overall blend. Finally, the presence of PO introduces a dilution effect, weakening the interfacial adhesion between the rubber and thermoplastic phases. This diminished adhesion reduces the material's capacity to bear mechanical loads, further contributing to the observed decline in tensile strength.

At higher concentrations, PO causes the cross-linked networks within the rubber phase to swell due to oil absorption, while simultaneously plasticizing the PP phase. This swelling disrupts the phase morphology and diminishes the compatibility between the ENR and PP components, exacerbating the loss of mechanical integrity. Furthermore, larger oil volumes can induce more pronounced phase separation, further compromising the internal network structure of the TPV. These micro-structural changes account for the progressive decline in tensile properties observed with increasing PO content. These findings underscore the delicate balance between mechanical performance and processability in TPVs. While the addition of PO enhances processability and flexibility, as evidenced by the decreasing tension set trend in Figure 5(b), it inevitably comes at the cost of reduced tensile strength and hardness. This trade-off highlights the critical importance of optimizing plasticizer content to achieve the desired equilibrium between elastomeric performance and structural strength, particularly for industrial applications where tailored mechanical properties are essential.

Figure 5(b) also reveals that elongation at break increases significantly with rising PO content, peaking at around 30 phr, where it reaches approximately 400%. Beyond this optimal point, elongation at break declines steadily as the plasticizer content continues to increase. This trend suggests that moderate oil concentrations enhance the flexibility and stretchability of the TPV by softening the polymer matrix and ENR domains, thereby improving chain mobility. However, excessive oil disrupts the material's structural integrity, leading to reduced elongation. In conclusion, these findings highlight the dual role of PO as a plasticizer in ENR-20/PP TPVs, enhancing flexibility at moderate levels while compromising strength at higher concentrations. This study provides valuable insights into the behavior of thermoplastic elastomers and offers practical guidance for designing TPV formulations with tailored properties to meet specific industrial demands.

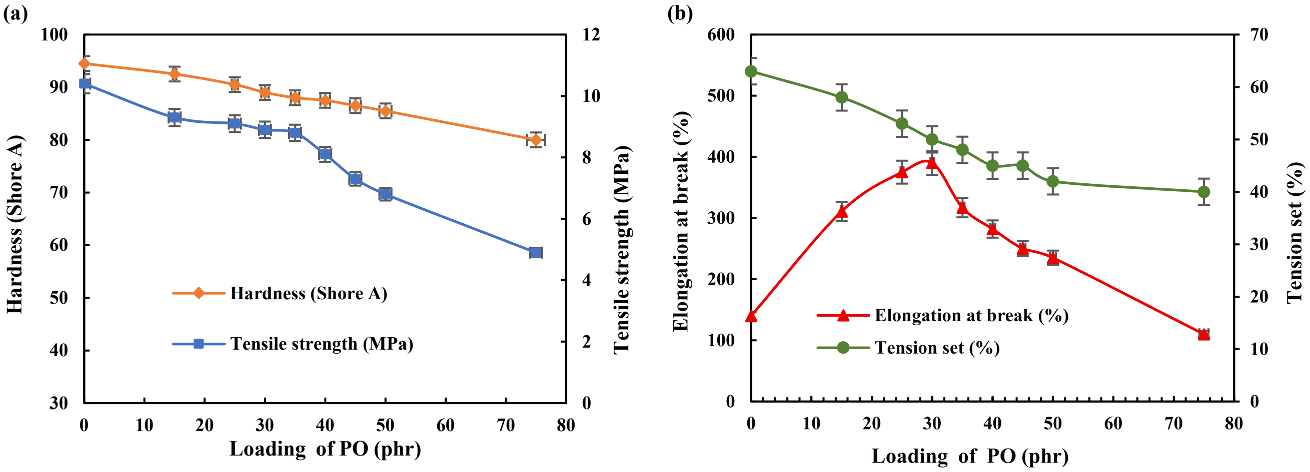

Figure 5. (a) Tensile strength and hardness, and (b) elongation at break and tension set of dynamically cured 60/40 ENR-20/PP blends with varying PO loadings.

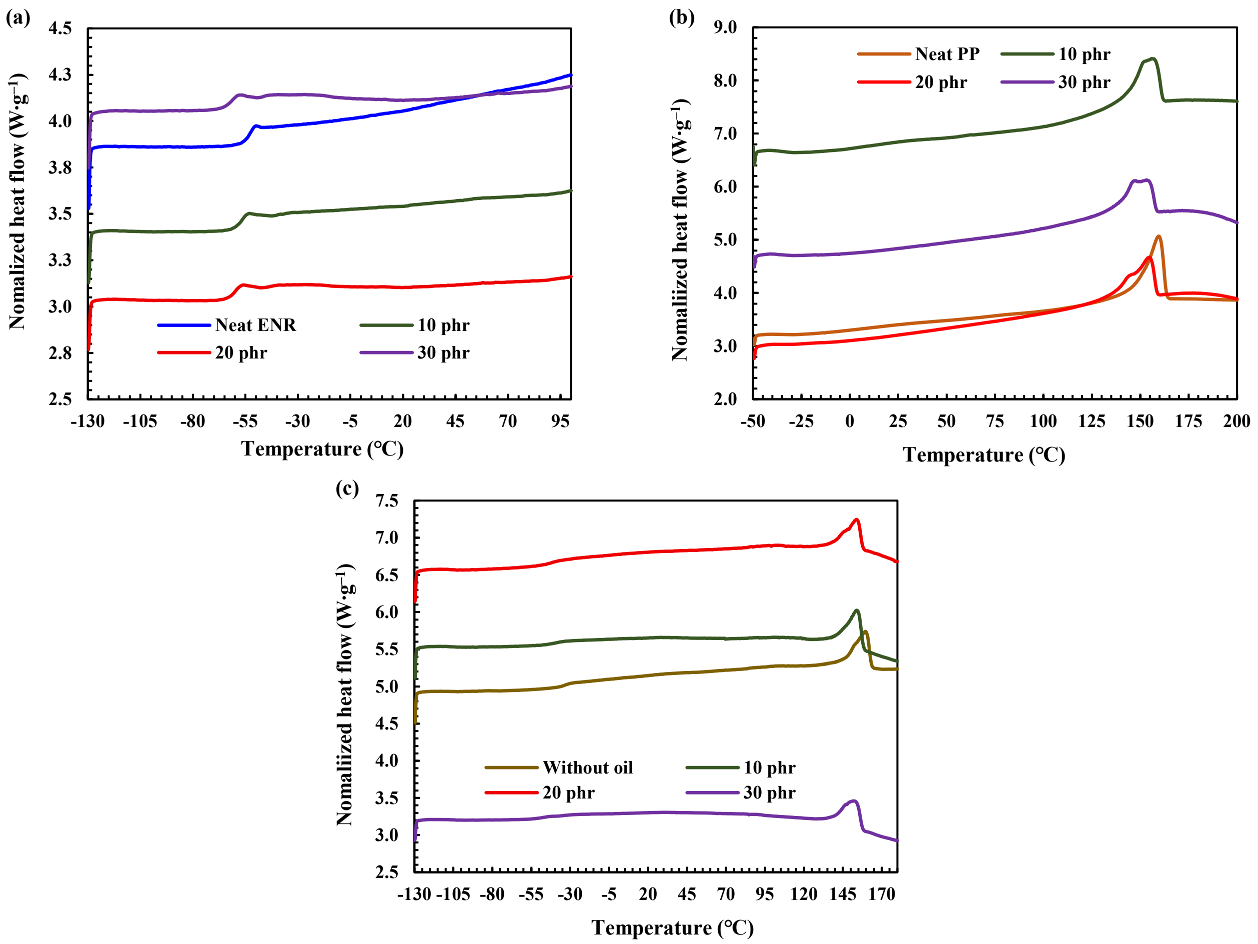

Figure 6. DSC thermograms of (a) ENR-20, (b) PP, and (c) dynamically cured 60/40 ENR-20/PP blends, each containing PO at levels of 0 (without oil), 10 phr, 20 phr, and 30 phr.

Figure 6(b) presents the DSC thermograms for neat PP and its modified forms containing different concentrations of PO at 10 phr, 20 phr, and 30 phr, over a temperature range of –50°C to 200°C. A prominent thermal transition is observed in all samples, marked by a peak in the 150°C to 160°C range, corresponding to the melting temperature (T_m) of crystalline regions in PP molecules, as summarized in Figure S3(b). The incorporation of PO causes the melting peak to broaden and decrease in intensity compared to neat PP. This broadening indicates partial disruption of the crystalline regions due to the presence of PO. As the PO concentration increases, the sharpness and intensity of the melting peak are further reduced, reflecting a progressive decrease in the crystallinity of PP (Figure 6(c)). This reduction in crystallinity is attributed to PO's role as a plasticizer, which interferes with the formation and stability of crystalline structures, resulting in a transition to a more amorphous and semi-crystalline phase with increased amorphous content. These findings align with similar observations in the literature, such as the decreased crystallinity of PP when crude palm oil is used as a plasticizer in increasing amounts [33].

Figure 6(c) presents the DSC thermograms for dynamically cured 60/40 ENR-20/PP blends, with PO concentrations of 0 phr, 10 phr, 20 phr, and 30 phr. Two distinct thermal transitions are evident: a low-temperature transition corresponding to the glass transition temperature (T_g) of the ENR phase, and a high-temperature transition associated with the melting temperature (T_m) of the crystalline PP phase in the ENR-20/PP TPVs. As illustrated in Figure S3(a-b), the T_g of the ENR phase in the ENR-20/PP TPVs is higher than that of unblended or neat ENR. This shift can be attributed to the presence of PO retained within the vulcanized ENR domains. The crosslinked network in the ENR phase hinders the ability of PO molecules to function effectively as lubricants or plasticizing agents for the molecular chains, thereby diminishing their flexibility compared to ENR blended solely with PO. Additionally, the T_m of the PP phase in the ENR-20/PP TPVs, shown in Figure S3(b), is marginally lower than that of neat PP. Although PO tends to diffuse into the PP phase under similar loading conditions, a portion of the oil preferentially remains within the ENR domains. This selective partitioning limits the amount of PO available to plasticize the PP phase in the blend, compared to pure PP with equivalent PO content, resulting in a slight reduction in T_m. A similar decrease in T_m for the PP phase with plasticizer incorporation has been reported in PP/EPDM TPVs [34]. Overall, both the T_g of the ENR phase and the T_m of the PP phase in ENR-20/PP TPVs exhibit a downward trend relative to their individual, unblended counterparts. This behavior is primarily attributed to the plasticizing effect of the PO, as previously discussed.

The plasticization and lubrication effects within both the ENR and PP phases play a crucial role in determining the degree of crystallinity, as illustrated in Figure S3(c). The crystallinity of the PP phase decreases with increasing PO content, a trend that correlates with the observed reduction in the strength properties of TPVs. This aligns with prior studies demonstrating that plasticizers reduce stiffness, strength, and hardness (Figure 3 and Figure 5(a)) through their plasticizing effect on both the PP phase and ENR domains, enhancing the material's low-temperature performance. A similar decline in crystallinity and T_m of the PP phase has been reported in NBR/PP TPVs with various types of non-polar and polar plasticizers and oils [35]. Interestingly, the crystallinity of the PP phase in the ENR-20/PP blend is lower than that of neat PP, even though the PP phase in the ENR-20/PP blend retains less PO. This phenomenon can be attributed to the dynamic vulcanization process, which introduces mechanical and thermal stresses as well as chemical interactions, particularly within the ENR domains and at the interfaces. These factors disrupt the ability of PP chains to align and form regular crystalline structures, thereby reducing the degree of crystallinity and altering the material's strength properties.

3.3 Influence of fillers on the properties of PO-plasticized ENR-20/PP TPVs

Figure 7 illustrates the stress-strain behavior of dynamically cured 60/40 ENR-20/PP blends containing 30 phr PO with varying loadings of carbon black and silica fillers. It is noted that a PO content of 30 phr was selected for the formulation due to its optimal balance between mechanical performance and processability. Specifically, the ENR-20/PP TPV containing 30 phr of PO exhibited the highest elongation at break and a low tension set value, indicating superior elasticity and recovery characteristics (Figure 4(b)). Increasing the PO content beyond 30 phr led to further matrix softening and a noticeable decline in tensile strength and hardness, primarily due to excessive plasticization and phase separation. The addition of fillers (carbon black and silica) significantly enhances the stress at break (i.e., tensile strength) compared to the unfilled blend, as shown in Figure 8(a). The tensile strength increases with filler loading, and for a given concentration, carbon black imparts slightly higher tensile strength than silica. This observation is consistent with studies on carbon black and silica-reinforced natural rubber vulcanizates [36]. This variation in reinforcement efficiency between carbon black and silica can be ascribed to their differing surface chemistries, which govern their interactions with the polymer matrix, as well as their preferential localization within either the plastic or rubber phase during dynamic vulcanization [17]. Regarding elongation at break, Figure 7 and Figure 8(b) reveal that both silica and carbon black enhance this property at lower filler loadings, up to approximately 30 phr. This improvement is likely due to enhanced interfacial bonding between the polymer matrix and the fillers, which enhance stress transfer while maintaining flexibility and improving elongation. A peak in elongation at break is observed around 30 phr for both fillers, indicating an optimal balance between reinforcement and stress-absorbing effects. Beyond this threshold, elongation at break decreases as filler agglomeration and increased composite rigidity hinder polymer chain mobility, thereby reducing extensibility. Interestingly, silica demonstrates a higher elongation at break than carbon black, particularly near the optimal filler loading of 30 phr. This suggests that silica exhibits better compatibility with the polymer matrix or provides more efficient stress dispersion, leading to superior extensibility under specific conditions. Therefore, silica at 30 phr was selected as the optimal filler loading because it provided the best balance of reinforcement and elasticity, yielding the highest elongation at break and lowest tension set without causing excessive stiffness.

The increasing trend in elongation at break at low filler loadings for both filler types, as depicted in Figure 8(b), corresponds to the decreasing tension set values, reaching a minimum at 30 phr (Figure 8(c). This reflects the enhanced elasticity of the TPV samples. Beyond 30 phr, however, the tension set exhibits a slight increase, accompanied by a reduction in elongation at break. Notably, TPVs filled with silica demonstrate lower tension set values at equivalent loading levels, indicating superior rubber elasticity compared to those filled with the same quantity of carbon black. This behavior can be attributed to the stronger polar interactions between silica (further enhanced by silane coupling agents) and the polar epoxidized groups in ENR. These interactions facilitate more uniform dispersion of silica, allowing it to predominantly reside within the ENR matrix [37]. This, in turn, improves stress transfer and enhances chain mobility. Additionally, the silane coupling agent used in this study, Bis(3-triethoxysilylpropyl) tetrasulfide, plays a crucial role in enhancing interfacial compatibility between the polar silica surface and the ENR matrix. During compounding, the ethoxy groups hydrolyze and react with hydroxyl groups on the silica surface, forming stable siloxane bonds. Simultaneously, the tetra-sulfide functional group can participate in the sulfur vulcanization of ENR, forming covalent linkages with the rubber chains. This dual-reactivity promotes strong interfacial bonding, improves filler dispersion, and reduces agglomeration, thereby contributing to enhanced mechanical properties and elastic recovery of the TPVs. Conversely, carbon black forms less interactive and more rigid filler networks, which restrict chain mobility, increase stiffness, and ultimately result in reduced elongation at break and higher tension set, as illustrated in Figure 8(c).

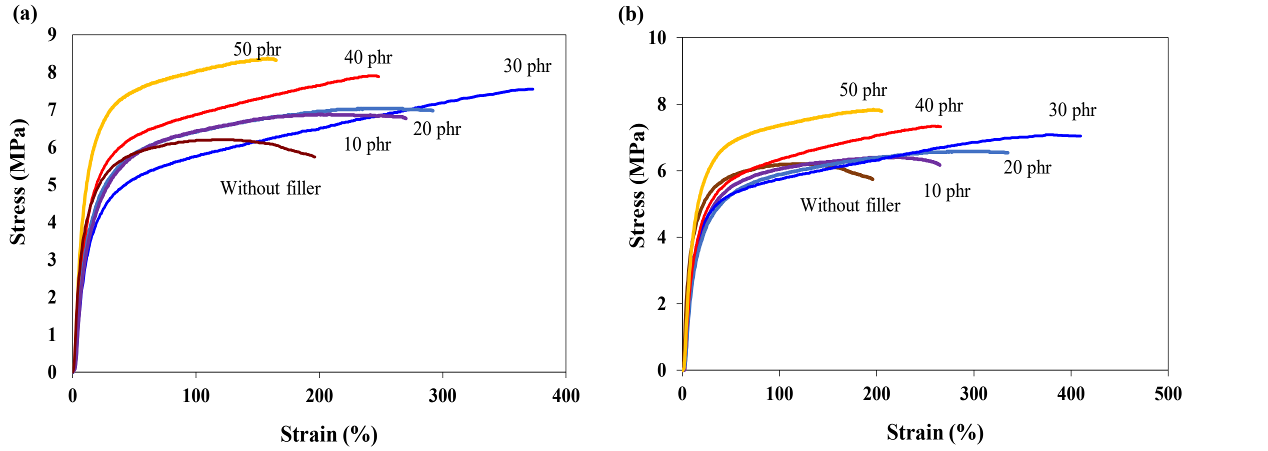

Figure 7 Stress-strain relationship of dynamically cured 60/40 ENR-20/PP blends with 30 phr of PO and varying carbon black (A) and silica (B) loadings.

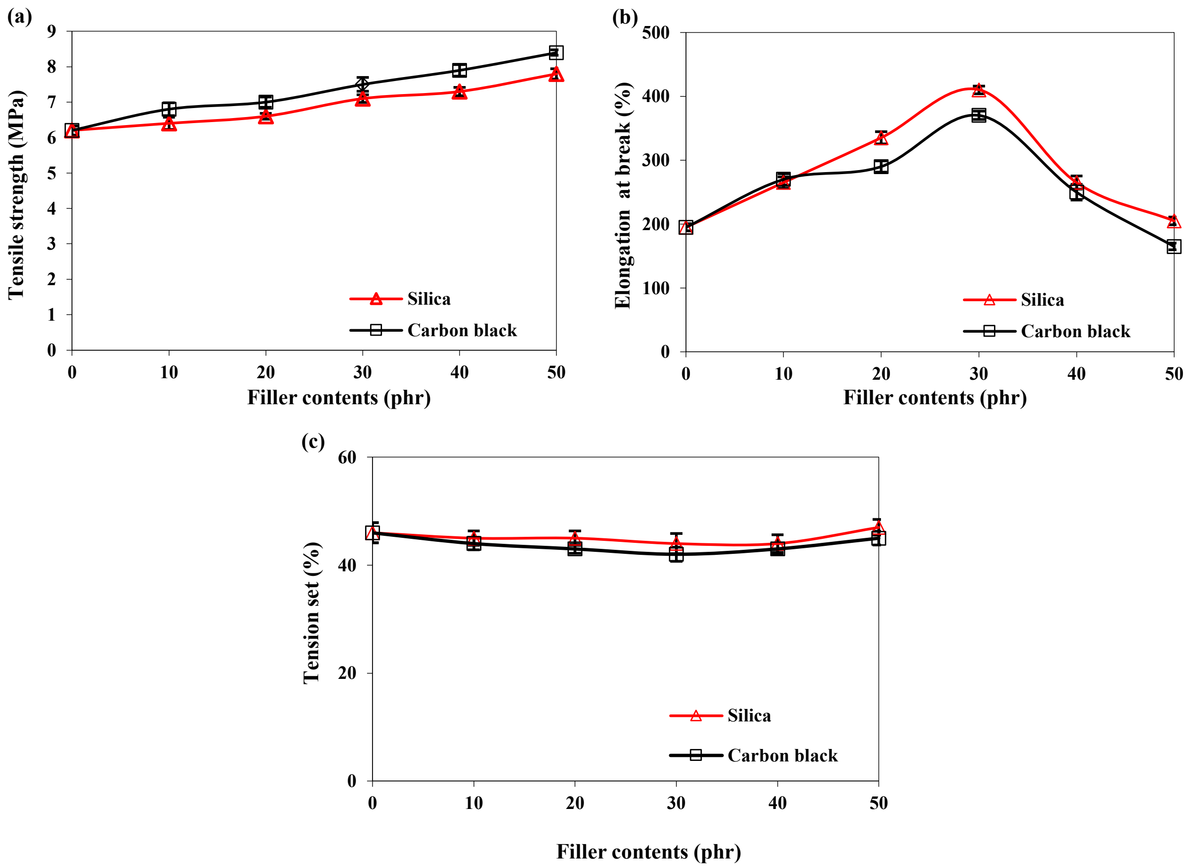

Figure 8. (a) Tensile strength, (b) elongation at break, and (c) tension set of dynamically cured 60/40 ENR-20/PP blends with 30 phr of PO and varying carbon black (a), and silica (b) loadings.

Figure S4 (in the supplementary information) presents the DSC thermograms of 60/40 ENR-20/PP blends containing 30 phr PO and 30 phr of either carbon black or silica. The thermal properties derived from these thermograms, including the glass transition temperature (T_g) of the ENR phase, the crystalline melting temperature (T_m) of the PP phase, and the degree of crystallinity of the PP phase in ENR-20/PP TPVs, are summarized in Table 2. The results indicate that the incorporation of fillers, in the presence of 30 phr of PO, leads to a slight increase in the T_g of the rubber phase and the T_m of the PP phase. Furthermore, the degree of crystallinity shows a modest increase, likely due to the fillers acting as nucleating agents that promote the formation of new crystalline structures in the PP phase during the blending process [38–40]. This increase in crystallinity can be attributed to the heterogeneous nucleation effect provided by both carbon black and silica particles. These fillers offer high-surface-area sites that reduce the activation energy barrier for nucleation, facilitating the formation of crystalline structures during cooling. As a result, the crystallization rate of the polypropylene phase is enhanced, leading to a higher degree of crystallinity (X_c), as observed in Table 2. Notably, silica, especially when well-dispersed through silane treatment, can further amplify this effect due to improved interfacial interaction with the polymer matrix. The increase in crystallinity contributes to improved thermal resistance and dimensional stability of the TPVs, which is beneficial for performance in demanding applications. Therefore, both fillers (carbon black and silica) significantly influence the thermal properties of the ENR-20/PP blends by enhancing thermal stability and altering the crystallization and melting behavior. Notably, silica exerts a slightly greater effect compared to carbon black, which may be attributed to its superior compatibility or dispersion within the polymer matrix. These findings align well with the mechanical and elastic properties described in Figure 7–8.

3.4 Influence of blend ratios on the properties of PO-plasticized silica-filled ENR-20/PP TPVs

Figure 9 depicts the stress-strain behavior of dynamically cured ENR-20/PP blends containing 30 phr of PO and 30 phr of silica at varying blend ratios. An initial sharp increase in stress is observed, followed by either a plateau or a gradual rise, depending on the blend proportions of 40/60, 50/50, 60/40, and 75/25 ENR-20/PP blends. In PP-rich blends (i.e., 25/75 and 40/60 ENR-20/PP), the yield point is characterized by a peak in maximum stress, followed by a gradual decline. This behavior reflects the dominant influence of the PP phase, as evidenced by the highest tensile strength and brittle characteristics observed in the 25/75 ENR-20/PP TPV. These brittle properties are further supported by the slope of the curve, which corresponds to the modulus.

The strength properties of ENR-20/PP TPVs decrease with reduced PP content or increased ENR proportion, as shown in Figure 10(a). Conversely, higher ENR content enhances elongation at break, peaking at approximately 510% in the 40/60 ENR-20/PP TPV. Increasing the ENR content beyond 60 wt% leads to a decline in elongation at break, reaching a minimum of approximately 85% in the 25/75 ENR-20/PP TPV, as shown in Figure 10(b). These findings suggest that the mechanical properties of ENR-20/PP TPVs are influenced by various factors, including the compatibility between the ENR and PP phases. Dynamic vulcanization facilitates the formation of crosslinked ENR domains dispersed within the PP matrix, supported by interfacial adhesion through interactions between the PP and ENR phases via the links by phenolic-modified PP compatibilizer [22]. It is noted that dynamic vulcanization facilitates the formation of crosslinked ENR domains dispersed within the PP matrix. This process is highly influenced by the shear forces applied during melt mixing. In our case, the Brabender mixer operated at a rotor speed of 80 rpm, providing sufficient shear to break up the vulcanizing ENR phase into fine domains. The torque profile observed during mixing shows a progressive increase followed by a plateau, indicating the formation of a stable crosslinked network. These shear and torque conditions not only promote fine dispersion but also help stabilize the morphology, resulting in uniformly distributed crosslinked ENR domains, as confirmed by SEM micrographs. This revolution of morphology has been clearly described in our previous report [41]. Additionally, the plasticizer, filler, and blend ratio significantly affect the mechanical properties and are closely linked to the final phase morphology of the ENR-20/PP TPVs, as demonstrated in Figure 11. It is observed that the 50/50 ENR-20/PP TPV exhibits the smallest vulcanized rubber domains dispersed in PP matrix and a high elongation at break of approximately 450%. This is attributed to the interfacial adhesion between the ENR domains and the PP matrix, which is further enhanced by the plasticizing effect of PO and silica reinforcement. The 40/60 ENR-20/PP TPV achieves the highest elongation at break, approximately 510%, which may be associated with the synergistic effect of the yielding behavior of the PP phase. This also corresponds to the presence of larger vulcanized rubber domains compared to those in the 50/50 ENR-20/PP TPV blend. In contrast, ENR-rich (75/25) and PP-rich (25/75) TPVs exhibit larger phase morphologies. In the ENR-rich blend, this is attributed to the lower shear viscosity during vulcanization, which limits the breakup of the vulcanizing ENR phase. In the PP-rich blend, the large amount of vulcanizing ENR phase fails to fully disperse into micro-sized vulcanized rubber domains within the PP matrix. These blend ratios also fail to form a co-continuous phase morphology an intermediate before transitioning to a dispersed or sea-island morphology [41]. This behavior is primarily due to the viscosity mismatch between the components during blending [42]. Furthermore, as illustrated in Figure 10(c), the elasticity of the TPV materials decreases with increasing PP content, as evidenced by the rise in tension set.

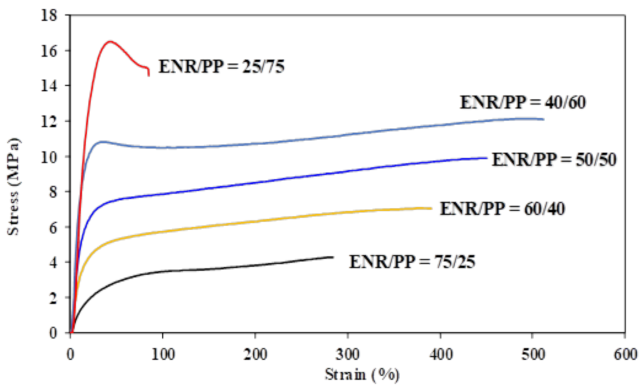

Figure 9. Stress-strain behavior of dynamically cured ENR-20/PP blends containing 30 phr of PO and silica (Ultrasil VN3) with varying blend proportions.

Table 2. Glass transition temperature (T_g) of ENR, crystalline melting temperature (T_m) of PP, and degree of crystallinity (X_c) of PP in dynamically cured ENR-20/PP blends.

Filler type	T_g of ENR phase [°C]	T_m of PP phase [°C]	X_c of PP phase [%]
Without filler	–49.0	152	19.8
Carbon black	–46.0	155	20.1
Silica	–48.0	154	20.2

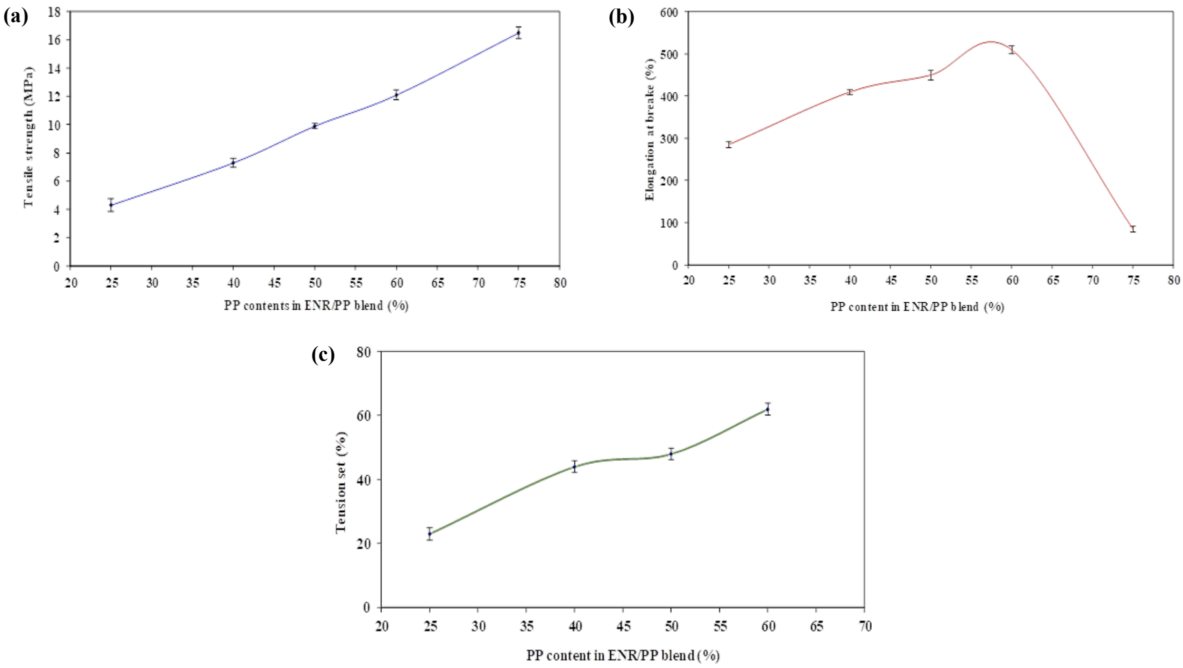

Figure 10. (a) Tensile strength, (b) elongation at break, and (c) tension set of dynamically cured ENR-20/PP blends containing 30 phr of PO and 30 phr of silica (Ultrasil VN3) with varying blend proportions.

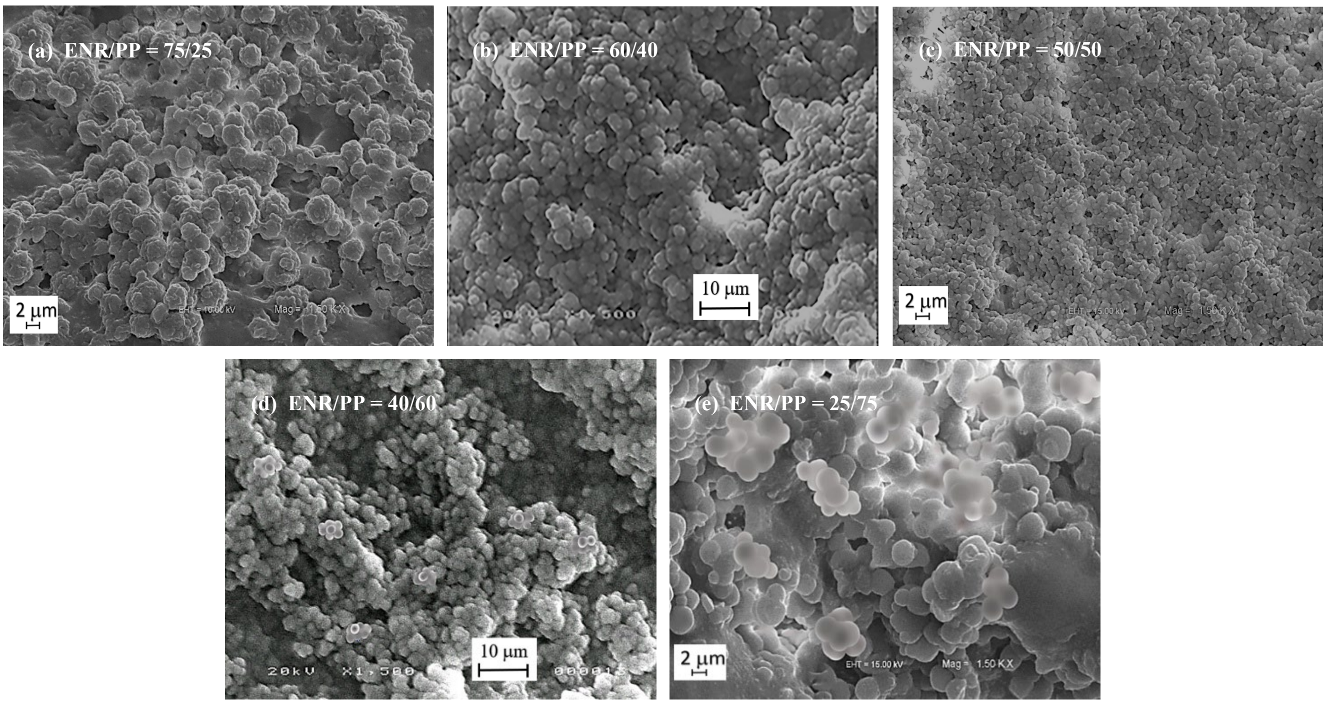

Figure 11. SEM micrographs of dynamically cured ENR-20/PP blends with 30 phr of PO and 30 phr of silica (Ultrasil VN3) at varying blend proportions.

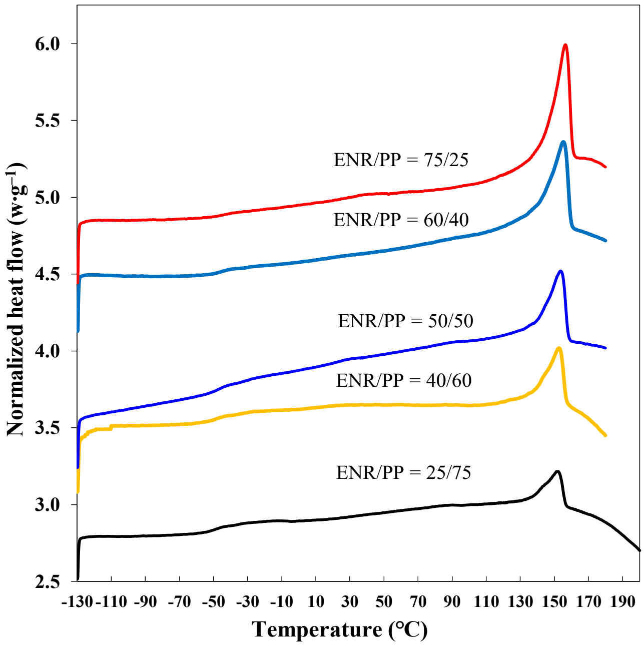

Figure 12. DSC thermograms of dynamically cured ENR-20/PP blends with 30 phr of PO and 30 phr of silica (Ultrasil VN3) at varying blend proportions.

Figure 12 presents the DSC thermograms of dynamically cured ENR-20/PP blends containing 30 phr of PO and silica across varying blend ratios. These thermograms provide valuable insights into key thermal properties, including the glass transition temperature (T_g) of the ENR phase, the crystalline melting temperature (T_m) of the PP phase, and the degree of crystallinity (X_c), which are comprehensively summarized in Figure S5 (in the supplementary information). A noteworthy trend is observed in the T_g of the ENR phase, which increases with a higher proportion of PP. This behavior is attributed to reduced chain flexibility in the ENR phase, aligning well with the tension set results illustrated in Figure 10(c).

Moreover, the increase in both the crystalline melting temperature (T_m) and the degree of crystallinity (X_c) with higher PP content in ENR-20/PP TPVs can be attributed to several factors.The higher proportion of PP introduces a larger volume of crystalline regions, as PP is inherently a semi-crystalline polymer. This promotes efficient packing of PP chains into an ordered structure during cooling, thereby enhancing X_c. The melting and crystallization behavior of isotactic polypropylene observed here closely parallels that reported in NBR/PP blends [43]. Additionally, the dynamic vulcanization process likely facilitates improved phase separation between the ENR and PP phases, enabling the PP phase to crystallize more effectively without significant interference from the amorphous ENR phase. The observed increase in T_m reflects the formation of thermally stable crystalline regions, which may also result from the enhanced nucleation density induced by silica particles. That acts as nucleating agents, promoting crystallization within the PP phase and further enhancing its thermal stability and mechanical strength. These findings underscore the complex interplay between blend composition, filler reinforcement, and dynamic vulcanization. Together, these factors significantly influence the thermal and mechanical properties of ENR-20/PP TPVs, providing valuable insights for tailoring material performance for specific applications.

4. Conclusion

This study provides a comprehensive analysis of dynamically cured ENR-20/PP TPVs, emphasizing the optimization of plasticizers, fillers, and blend ratios to achieve superior material properties. Among the tested plasticizers, paraffinic oil emerged as the most effective, significantly enhancing the flexibility, elongation, and processability of TPVs while maintaining acceptable tensile strength and hardness. The reinforcement effects of carbon black and silica fillers were distinct, with silica demonstrating superior compatibility and elasticity improvements due to its strong interaction with the polar epoxidized natural rubber (ENR) matrix. Optimized blend ratios revealed a delicate balance between the rubber and plastic phases, with ENR-20/PP ratios of 40/60, 50/50, and 60/40 exhibiting a desirable combination of mechanical strength, flowability, and elasticity. These enhancements were attributed to fine phase morphology and strong interfacial adhesion between phases. In particular, the 40/60 blend ratio yielded a maximum elongation at break of approximately 510%, demonstrating superior flexibility. Thermal analyses further highlighted the impact of plasticizers and fillers on crystallinity and thermal transitions, leading to improved low-temperature performance and flexibility. This research underscores the critical role of strategic selection and precise loading of additives and blend ratios in tailoring ENR-20/PP TPV properties for specific industrial applications. The findings advance TPV material design, offering pathways for their use in demanding applications requiring a balance of durability, flexibility, and thermal stability. These property improvements position the optimized ENR-20/PP TPVs as promising candidates for automotive elastomeric components, flexible consumer goods, and vibration-damping applications. However, the current study is limited to laboratory-scale evaluations under controlled conditions. Future work should investigate long-term aging, thermo-oxidative stability, and performance under service conditions to validate industrial applicability of the optimized TPVs.

Acknowledgments

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