

The effect of polyvinyl chloride and polyethylene terephthalate on the mechanical properties of butyl rubber (IIR)-based thermoplastic elastomer using semi-efficient vulcanisation system and a nano zinc oxide as activator

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Abstract

Thermoplastic elastomers (TPEs), a class of materials bridging the gap between rubber and thermoplastics, have revolutionised diverse fields with their unique properties and applications. This study highlights the critical importance of compatibility between plastics, polyvinyl chloride (PVC), polyethylene terephthalate (PET), and butyl rubber (isobutylene-isoprene rubber, IIR) components in TPEs for optimal performance. Several TPEs were prepared with different amounts of plastics. Subsequently, the TPEs were cured, and curing and mechanical properties, and correspondent thermal stability and solvent resistance were measured. It revealed that the thermal stability of TPEs, containing PVC, PET and IIR, was influenced by the type and quantity of each plastic, affecting degradation temperatures. PVC and PET exhibited distinct effects on the curing behaviour of IIR-based TPEs, impacting scorch time and optimum cure time differently. The incorporation of PVC and PET enhanced the organic solvent resistance of the TPEs, attributed to physical barrier effects, enhanced crosslinking, increased crystallinity, and specific interfacial interactions. Tensile strength and elongation at break generally decreased with the addition of plastics, reflecting incompatible interactions and increased crystallinity. Meanwhile, hardness increased due to the rigid structure and filler effects of plastics. Achieving an optimal TPE formulation involves balancing these competing effects.

Keywords

TPE, IIR, PVC, PET, mechanical properties, thermal stability, solvent resistance

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Introduction

Thermoplastic elastomers (TPEs), a class of materials bridging the gap between rubber and thermoplastics, have revolutionised diverse fields with their unique properties.¹ Their journey, over a century, is marked by continuous innovation, versatile preparation methods and ever-expanding applications.² TPEs can be precisely engineered to exhibit specific properties such as elasticity, strength, heat resistance and weatherability, catering to diverse needs. In contrast to traditional rubber, TPEs allow for intricate shapes and complex designs through techniques such as injection molding.³ They offer superior resistance to wear, tear and abrasion compared to many other materials, extending product end-life and subsequently reducing waste. Many TPEs withstand exposure to oils, solvents and chemicals, making them suitable for demanding environments.⁴ Most TPEs, unlike thermoset rubbers, are

recyclable, thereby minimising environmental impact and fostering a circular economy. The growing availability of TPEs derived from renewable resources, such as corn starch and plant oils, further promotes eco-friendly material choices.⁵ Additionally, TPEs often require less processing time and energy compared to rubber, translating to lower manufacturing costs. TPEs have become indispensable in various daily applications, including footwear, electronics, automotive components, medical devices, sealing and gaskets.⁶

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The preparation of TPEs employs various techniques selected based on the desired properties and target application. The most common method is 'melt blending', where different polymers are physically mixed in a molten state using extruders or mixers.⁷ Another technique, 'solution mixing', involves dissolving polymers in a solvent, followed by casting or precipitation to obtain the final TPE form.⁸ While this method allows for intricate shapes and high product consistency, it may involve solvent recovery and environmental considerations. 'Reactive extrusion' combines melt processing with chemical reactions in the extruder, enabling real-time tailoring of TPE properties.⁹ In the 'grafting' technique, pre-existing polymers undergo chemical modification by attaching chains of another polymer, resulting in TPE-like properties.¹⁰ This method allows for incorporating specific functionalities while retaining the base polymer's characteristics. 'In situ polymerisation' involves directly polymerising monomers within another polymer matrix to create a TPE structure.¹¹ While offering precise control over morphology and properties, this method may require specialised equipment and techniques.¹² Researchers continually explore new and innovative techniques for preparing TPEs, including using bio-based materials, incorporating self-healing capabilities and introducing conductive functionalities to achieve desired TPE properties.⁴

Butyl rubber (isobutylene-isoprene rubber, IIR) is extensively employed in applications that demand exceptional air impermeability and outstanding damping properties.^{13,14} Its low gas permeability makes it well-suited for use in inner tubes, sealing applications and pneumatic tires. The vibration-damping characteristics of IIR contribute to its incorporation in automotive components and materials designed for noise reduction.¹⁵ In addition to its low gas permeability, IIR displays chemical resistance to alcohols, ketones and certain acids.¹⁶ It is essential to note, however, that its resistance to oils and strong oxidising agents is limited, warranting careful consideration in various applications. In response to this limitation, the strategy of blending IIR with other polymers (plastics) has emerged as an appropriate approach to enhance its properties for specific applications.

Polyvinyl chloride (PVC) is the third plastic in worldwide plastic production, followed by polyethylene and polypropylene.¹⁷ In 2016, its global production capacity hit 61 million metric tons, and its market value increased from 24.39 billion dollars in 2020 to 29.56 billion in 2021, boasting a 21.2% annual growth rate. This plastic comes in two forms, rigid and flexible. The flexible one owes its flexibility to the special plasticisers involved. Rigid PVC is used in construction applications, namely, pipes, doors and windows, and even molds plastic bottles, packaging, and bank cards. The flexible PVC is used in numerous applications, including plumbing, electrical wires and flooring.¹⁸ Pure PVC is a white, brittle material. While it won't dissolve in most solvents, it swells up in specific chlorinated ones. This contributes to its versatility, making it an important plastic across countless industries and applications. Polyethylene terephthalate (PET), a

polymer commonly known as PET, occupies the fourth position in global polymer production, surpassed only by polyethylene, polypropylene and PVC.¹⁹ This widespread utilisation and versatility are underscored by the remarkable 51 million metric tons of PET produced globally in 2021. The future of PET remains optimistic, fuelled by its remarkable adaptability, ongoing advancements in production techniques, and a growing emphasis on sustainable practices. The unique physicochemical properties and versatile nature of PET guarantee its continued presence in diverse applications, playing a key role in shaping the future of packaging, textiles and numerous other applications.²⁰ Limited research has been documented in the literature concerning IIR-based TPEs. Yao et al.²¹ conducted a comprehensive study on the microstructure, morphological evolution, corresponding mechanisms and properties of bromo-IIR (BIIR)/polypropylene thermoplastic vulcanisates. Their findings provided guidance for the development of high-performance TPEs tailored for industrial applications, particularly in the manufacturing of medical bottle stoppers. In another research endeavour,²² they studied the microstructure and properties of BIIR/PA 12 TPE, with a focus on creating recyclable inner liners for environmentally friendly tires. The aim was to contribute to the reduction of fuel consumption and carbon emissions in the tire manufacturing process. Tang et al.²³ embarked on the preparation of butyl rubber/polypropylene thermoplastic vulcanisates designed for shock-absorption devices through dynamic vulcanisation. They utilised octylphenolic resin as a vulcanising agent and investigated the morphological evolution and properties during the vulcanisation process. Previous studies^{24–26} have specifically concentrated on the preparation, formulation and mechanical properties of IIR/PA TPEs tailored for gas-barrier applications in tire inner liners. Guseynova et al.^{9,27} conducted several studies exploring the impact of concentrations of butyl rubber and dicumyl peroxide on the strength and thermophysical properties of polymer mixtures based on thermoplastic polyolefins. In a sustainable approach, Fazli et al.²⁸ utilised waste butyl rubber crumbs to produce TPE, showcasing an innovative recycling method for the development of environmentally friendly elastomeric materials. These studies collectively contribute to the expanding knowledge base on IIR-based TPEs and their diverse applications.

To the best of the authors' knowledge, a systematic study on PVC, PET, and their associated blends in butyl rubber-based TPEs has not been reported. This study aimed to fill this gap by employing a semi-efficient vulcanisation (SEV) sulphur curing system for IIR rubber compounds melt blended with varying amounts of PVC, PET and their blend (50–50) to produce TPE. The curing process incorporated the use of nano-zinc oxide (nZnO) as a curing activator, alongside two different accelerators, TBBS (N-tertiarybutyl-2-benzothiazole sulfenamide) and TMTD (Tetramethylthiuram sulfide). Each accelerator was assigned a specific role, with TMTD facilitating fast curing and TBBS ensuring safe-delayed action curing. Subsequently, a systematic evaluation of the rheological

and mechanical properties of the cured compounds was conducted, and the degradation behaviour was examined using thermogravimetry analysis (TGA). The obtained results underwent comprehensive comparative analysis. All assessments and measurements adhered to conventional techniques widely recognised in the rubber industry. This study not only contributes to the understanding of the interactions between butyl rubber and PVC, PET, or their blends but also sheds light on the potential applications and performance of the resulting TPEs.

Experimental

Materials – rubber, plastics and rubber curing chemicals

The materials employed in this investigation include:

1. IIR (butyl rubber): IIR-1675N obtained from SIBUR, Russia. This butyl rubber is characterised by 1.4 to 1.8 mol% unsaturation, with a Mooney viscosity (ML(1 + 4)125°C) ranging from 46 to 56.
2. PVC: PVC S65 sourced from Arvand Petrochemical Company, Iran. This PVC had an ash content of <0.1%, a density between 0.56 and 0.61 g/cm³, a viscosity number of 101 to 109 cm³/g, 20% to 25% crystallinity, number average molecular weight of 30000 g/mol, a glass transition temperature of 80 °C, and a porosity ranging from 19% to 25%.
3. PET: PET BG-821 (Bottle grade) acquired from Shahid Tondguyan Petrochemical Co., Iran. This PET type has an intrinsic viscosity (IV) of 0.82 dl/g, a melting point of 248°C, 30% to 40% crystallinity, number average molecular weight of 50000 g/mol, a glass transition temperature of 70°C, and a water content of less than 0.3%.
4. nZnO (Activator): Supplied by Arman Nanofanavar, Mashhad, Iran. It boasts 98% purity, with dimensions including a size and porosity of 60–70 nm and 6.5 nm, respectively. Its thermal stability is specified to reach up to 1120°C.
5. Santocure TBBS: A safe-processing delayed-action accelerator sourced from Woluwe, Belgium.
6. Tetramethylthiuram sulphide (Perkacit TMTD): A fast-curing activator obtained from Flexsys, Belgium.
7. Stearic Acid (SA, Co-Activator): Supplied by Anchor Chemical Ltd, UK.
8. Elemental sulphur (Curing Agent): Sourced from Solvay Barium Strontium, Hannover, Germany.

Preparation and vulcanisation of rubber compounds

The rubber (TPE) compounds were prepared using a two-roll mill (RHM-20, Iran) featuring rolls with a diameter of 15 cm and a length of 35 cm. A consistent 2 mm gap was maintained on the two-roll mill, and the cylinder rotation speed was set at 35 rpm. To control the temperature below 60°C throughout the mixing process, the mill was equipped with a cooling system. In the initial stage, IIR

Table 1. The formulation of rubber (TPE) compounds (all values in phr).

Compound number	RC	R0	R1	R2	Q0	Q1	Q2	S0	S1	S2	S3	
	R3	R4			Q3	Q4		S4				
IIR	100				100			100				
PVC	0	5	10	15	20			2.5	5	7.5	10	
		25								12.5		
PET					5	10	15	20	25	2.5	5	7.5
										12.5		

It is an SEV curing system (Accelerator/S = 1.3). All prepared compounds had 6, 2, 2, 2, and 3 phr, nZnO, stearic acid, TBBS, TMTD and sulphur in formulations, respectively.

IIR: isobutylene-isoprene rubber; PVC: polyvinyl chloride; PET: polyethylene terephthalate; TBBS: N-tertiarybutyl-2-benzothiazole sulfenamide; TMTD: tetramethylthiuram sulfide; SEV: semi-efficient vulcanisation; TPE: thermoplastic elastomer.

was masticated for 4 minutes before introducing plastics, PVC, PET or both (in case of a blend). The plastics were added into the masticated rubber (IIR) during a period of 6 minutes. After an additional 3 minutes of mixing the rubber and plastics mixture, curing chemicals were incorporated within 4 minutes, followed by a final mixing period of 3 minutes. As mentioned, the highest mixing temperature was controlled as 60°C. The formulation details of the prepared TPE compounds are elucidated in Table 1, configured as a SEV cure system, maintaining a weight ratio of the accelerator (TBBS + TMTD) to sulphur at 1.3. All prepared compounds included 6, 2, 2, 2, and 3 phr of nZnO, stearic acid, TBBS, TMTD, and sulphur in the formulations, respectively. Figure 1 visually represents the appearance of two selected compounds RC and R4 without plastics and with 25 phr PVC (Table 1) in formulations. Vulcanisation of the rubber compounds took place within a compression mold set at 160°C and a pressure of 150 atmospheres (bar), utilising optimal cure times (Table 2) determined from oscillating disc rheometer (ODR) cure curves (MDR-200B, SANTAM, Iran). Subsequently, sheets measuring 15 cm by 15 cm, with an approximate thickness of 2 mm, were employed for the evaluation of the mechanical properties of the cured rubber (TPE) compounds.

Measurement of rubber (TPE) compound cure properties

The scorch time (t_{s2}), optimum cure time (t_{90}) and Δ torque, indicative of crosslink density alterations in the rubber matrix, were determined through cure traces generated at a constant temperature of $160 \pm 2^\circ\text{C}$. This assessment was conducted using an ODR configured with a test frequency of 1.7 Hertz and a total running time of 60 minutes. The cure rate index (CRI) is calculated using: $CRI = 100 / (t_{90} - t_{s2})$. Detailed information on the cure properties of the formulated rubber compounds was provided in Table 2.

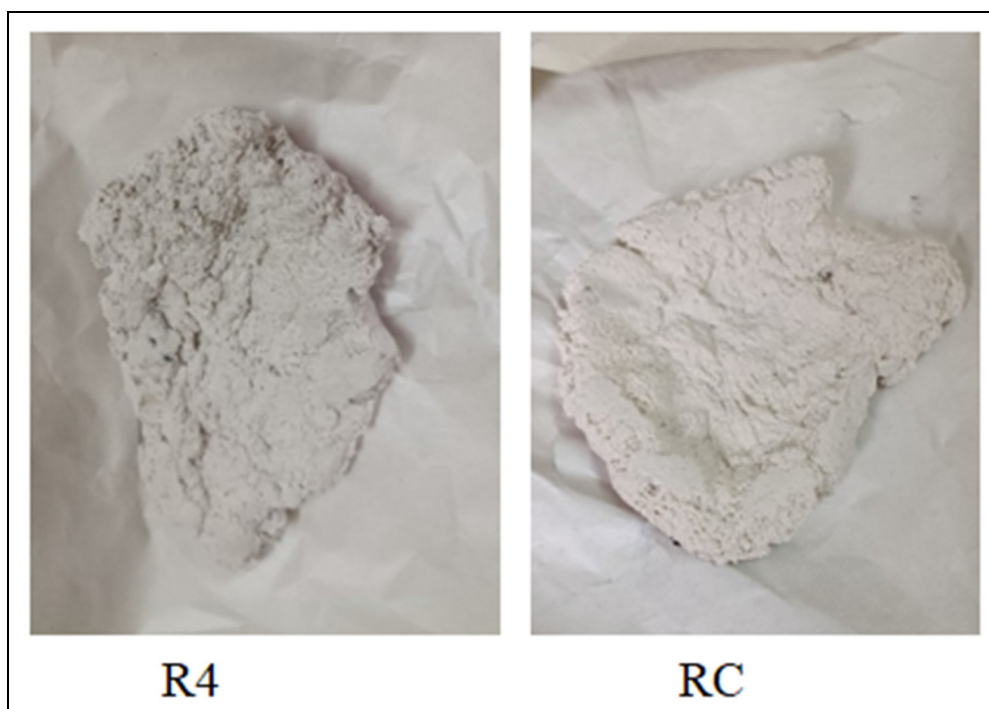


Figure 1. The appearance of two selected compounds RC and R4 without plastics and with 25 phr PVC in formulation (Table 1). PVC: polyvinyl chloride.

Table 2. Cure properties as determined by ODR for studied rubber (TPE) compounds.

Compound	t_{52} (min:sec)	t_{90} (min:sec)	Δ torque (dN.m)	CRI (1/s)
RC	4:40	10:24	3.4	0.30
R0	5:09	11:51	3.8	0.25
R1	5:33	10:25	3.8	0.33
R2	5:50	10:58	3.7	0.31
R3	6:03	12:10	3.8	0.26
R4	6:32	12:34	3.7	0.26
Q0	5:10	11:22	3.2	0.27
Q1	4:25	9:36	4.5	0.32
Q2	4:44	9:06	3.3	0.38
Q3	4:41	8:57	4.0	0.39
Q4	4:24	8:39	4.9	0.39
S0	5:55	10:27	2.8	0.28
S1	5:01	10:14	3.9	0.32
S2	5:24	10:38	4.0	0.32
S3	5:24	10:32	3.9	0.33
S4	5:15	10:39	4.2	0.31

CRI: cure rate index; ODR: oscillating disc rheometer; TPE: thermoplastic elastomer.

Measurement of thermal stability, crosslink density, tensile properties and hardness of cured rubber compounds

The thermal stability of the TPEs was evaluated using a thermogravimetry analyser (TGA, STA 1500, Scinco, South Korea) under an inert atmosphere of nitrogen gas. Figures 2 to 5 depict the TGA graphs for selected compounds RC, R4, Q4 and S4, without and with 25 phr of

plastics (PVC, PET and a 50–50 blend) in formulations (Table 1). Crosslink density (CLD) determination was carried out using toluene as the solvent. Rubber specimens of dimensions 1 cm by 1 cm were immersed in 40 mL of toluene in labelled containers for CLD determination. After a 72-hour swelling process at ambient temperature, the mass of the rubber samples was recorded daily until equilibrium. Following equilibrium, the solvent was extracted and the specimens underwent air drying for 9 hours, followed by additional drying in an oven at 85°C for 24 hours. A subsequent standing period of 24 hours at 23°C preceded the final reweighing. CLD was determined using the Flory–Rehner equation,¹³

$$V = -\frac{1}{V_s} \frac{\ln(1 - v_r^0) + v_r^0 + \chi(v_r^0)^2}{(v_r^0)^{1/3} - v_r^0/2} \quad (1)$$

where V is the CLD (mol/m^3), V_s the molar volume of toluene ($1.069 \times 10^{-4} \text{ m}^3/\text{mol}$ at 25°C), χ the interaction parameter ($\chi=0.557$), v_r^0 the volume fraction of rubber (polymer) in the swollen gel which was calculated using the following equation:

$$v_r^0 = \frac{1}{1 + \frac{d_r}{d_s} \left(\frac{1}{1 - f_{\text{fil}}} \right) \left(\frac{w_s}{w_0} - 1 \right)} \quad (2)$$

where d_r (1.15 g/cm^3) and d_s (0.867 g/cm^3) are the densities of the rubber and solvent, respectively; f_{fil} the initial weight fraction of filler in the sample (here =0) after double extractions by acetone and toluene; w_s the weight of the swollen gel and w_0 the weight of the dried sample. Figures 6 and 7 compare the swelling

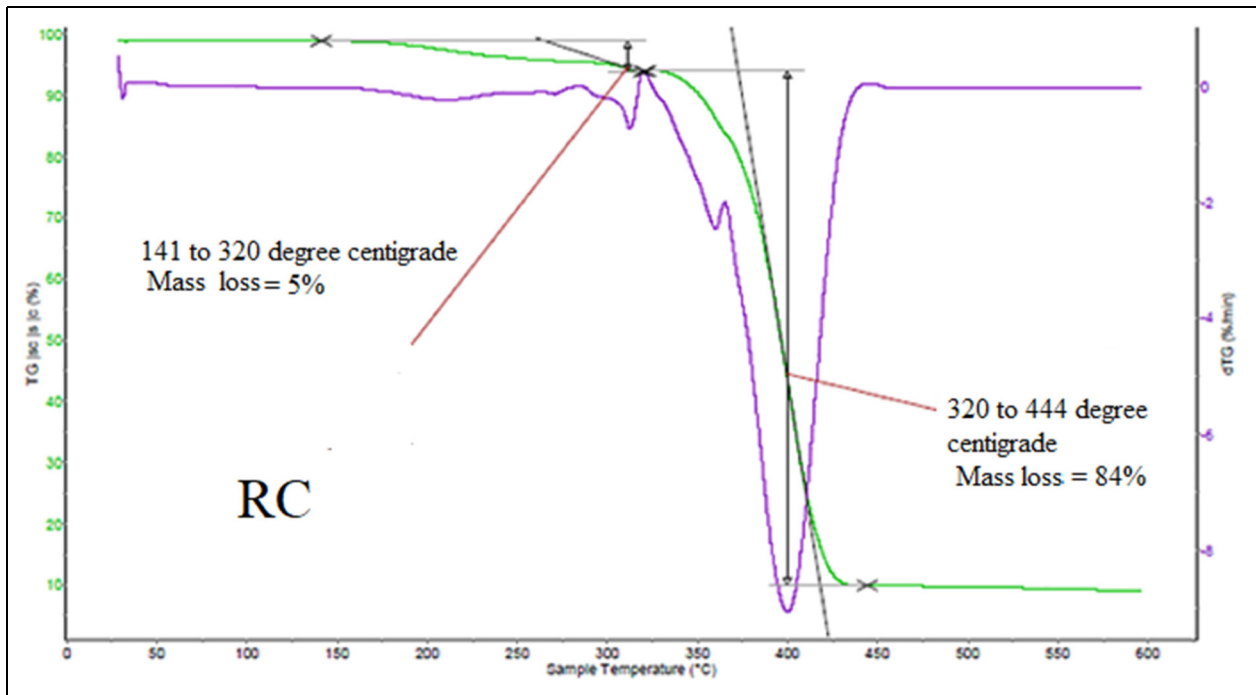


Figure 2. The TGA and DTGA graphs for reference compound, RC (Table I). DTGA: derivative thermogravimetric analysis; TGA: thermogravimetry analysis.

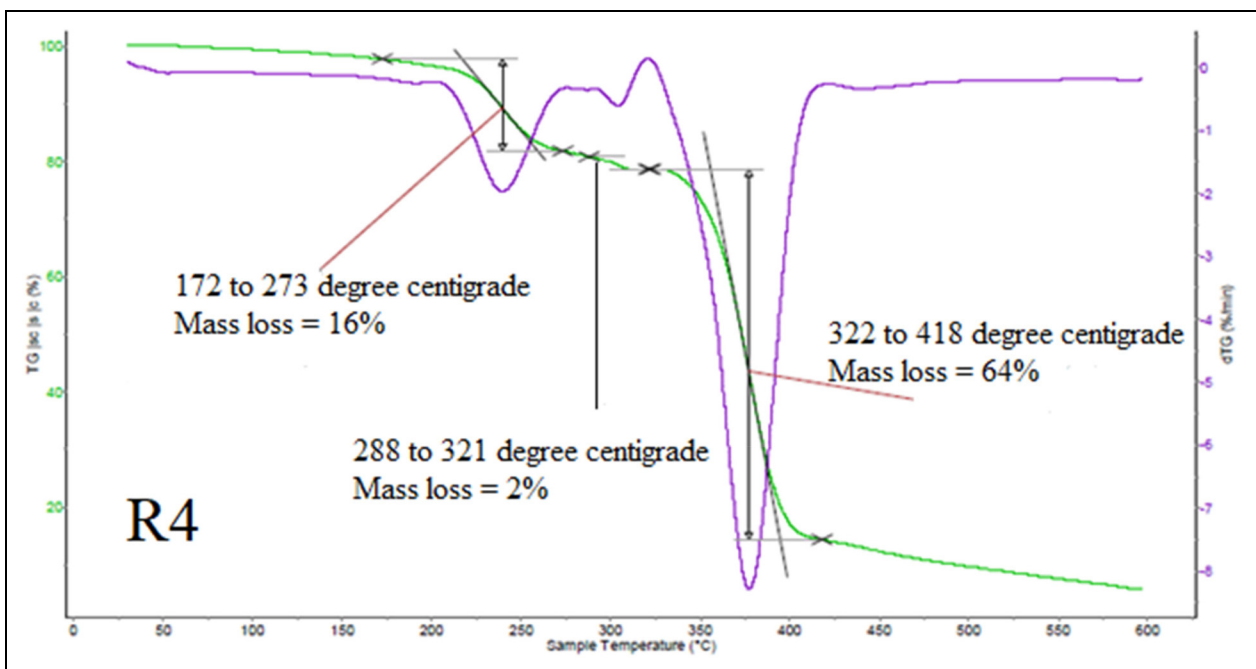


Figure 3. The TGA and DTGA graphs for compound R4 with 25 phr PVC in formulation (Table I). DTGA: derivative thermogravimetric analysis; PVC: polyvinyl chloride; TGA: thermogravimetry analysis.

percent's and CLDs of the prepared rubber (TPE) compounds, respectively. The mechanical properties, including tensile strength, elongation at break and hardness of the rubber compounds, were systematically evaluated using a uniaxial tension SANTAM STM-20 mechanical testing machine. Conventional dumbbell test pieces were employed as specimens. Hardness, measured in

shore A units, was determined using cylindrical samples with a thickness of 12.5 mm and a diameter of 29.0 mm. The mechanical testing experiments were conducted on five replicates to ensure reliability, and median values were reported to enhance precision. Table 3 provides a comparison of the mechanical properties of the selected rubber (TPE) compounds.

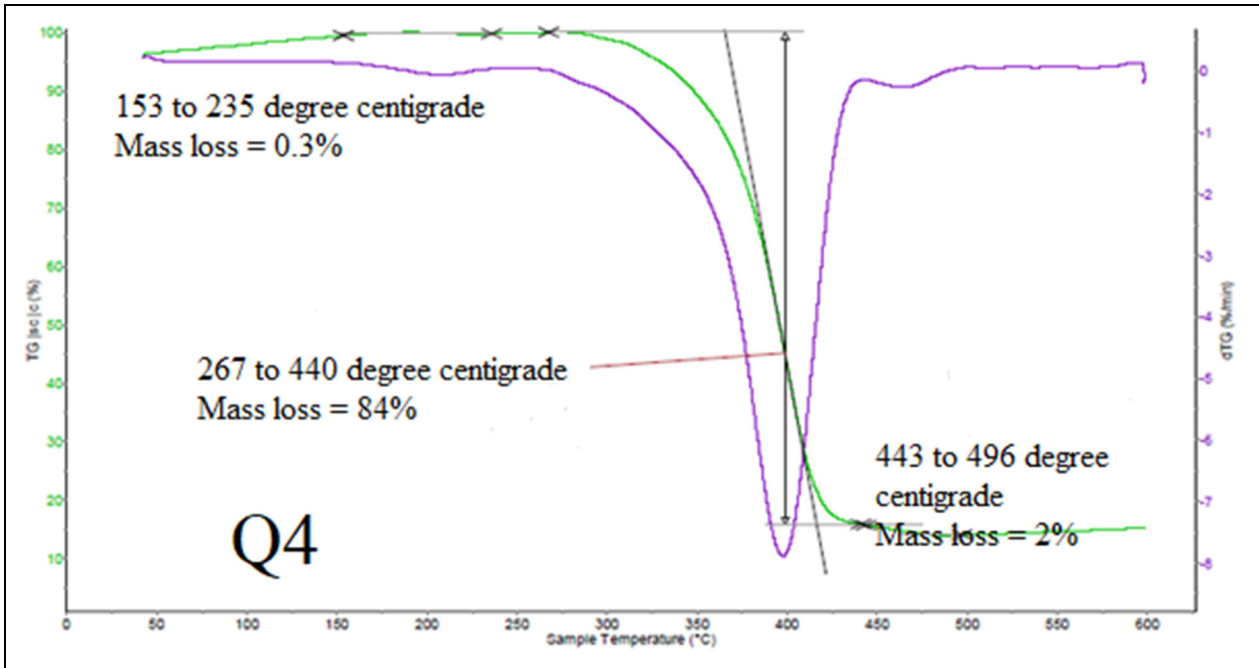


Figure 4. The TGA and DTGA graphs for compound Q4 with 25 phr PET in formulation (Table I). DTGA: derivative thermogravimetric analysis; PET: polyethylene terephthalate; TGA: thermogravimetry analysis.

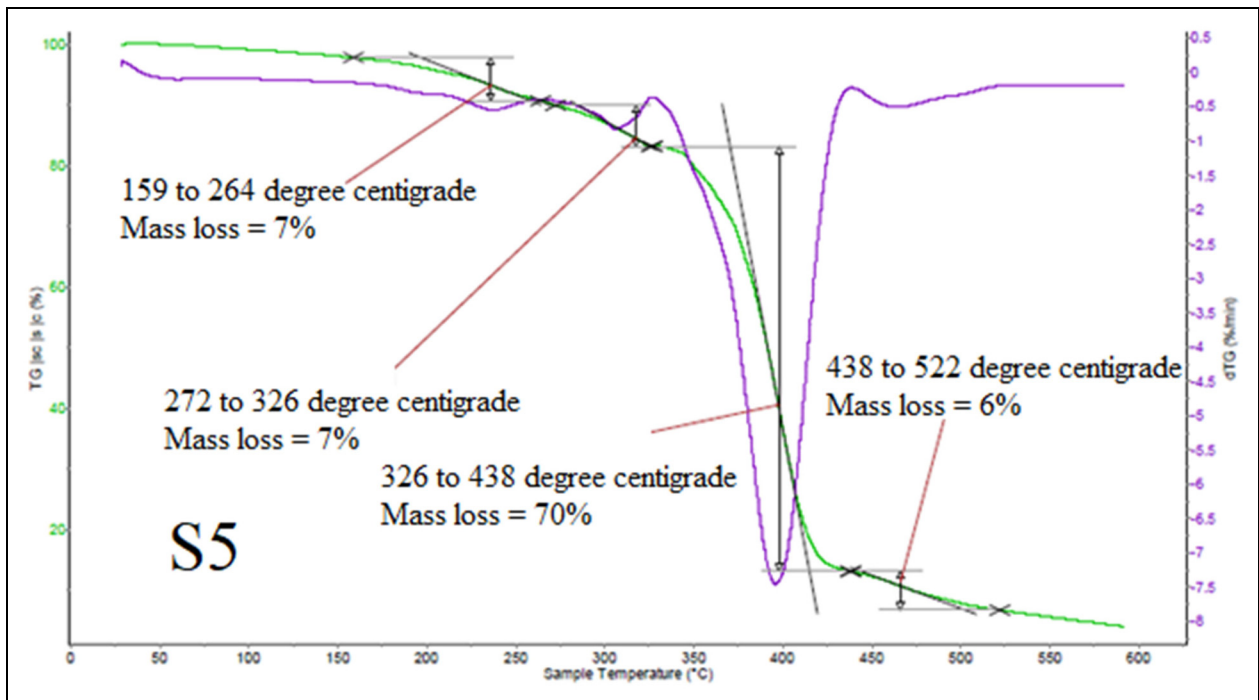


Figure 5. The TGA and DTGA graphs for compound S4 with 12.5 phr PVC and 12.5 phr PET in formulation (Table I). DTGA: derivative thermogravimetric analysis; PET: polyethylene terephthalate; PVC: polyvinyl chloride; TGA: thermogravimetry analysis.

Results and discussion

TPEs offer a synergistic combination of plastic and rubber properties, yet their effectiveness depends on achieving compatibility between these diverse polymers.²⁹ Incompatibility between the plastic and rubber components within a TPE structure can lead to blend heterogeneity, forming distinct

phases at the interface. This interface weakness adversely impacts the mechanical properties of the TPE, potentially resulting in poor adhesion and phase separation, rendering the material non-functional.³⁰ Processing challenges, such as difficulties in mixing, molding and extrusion, can arise due to poor interfacial adhesion, affecting the uniformity of

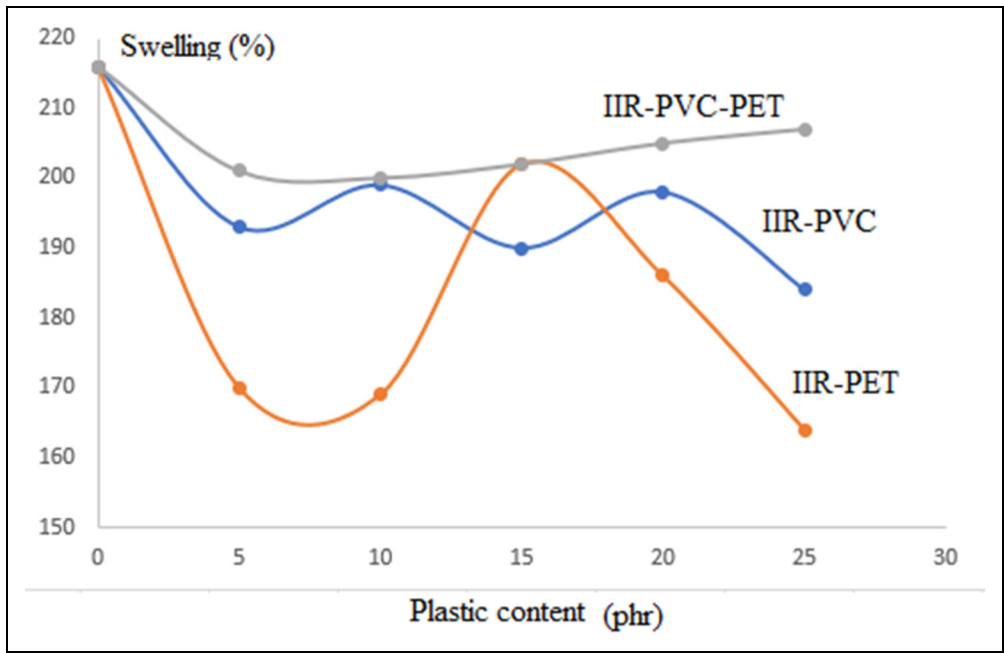


Figure 6. The comparison between swelling percent's in toluene for the prepared rubber (TPE) compounds. TPE: thermoplastic elastomer.

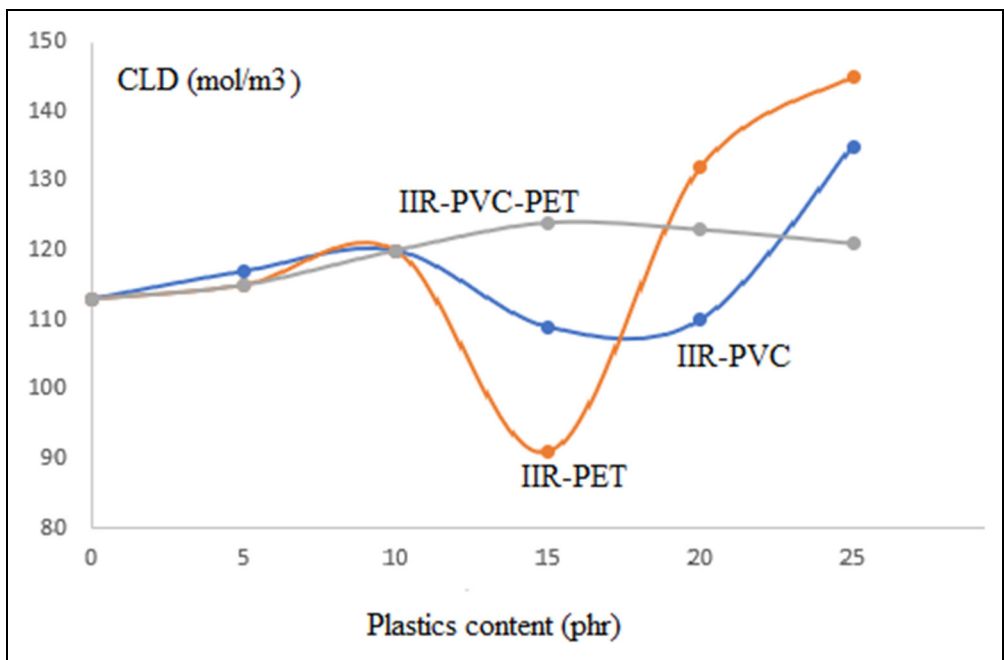


Figure 7. The comparison between CLDs of the prepared rubber (TPE) compounds. CLD: crosslink densities; TPE: thermoplastic elastomer.

Table 3. The mechanical properties of selected rubber compounds.

Compound number	Tensile strength (MPa)	Elongation at break (%)	Hardness (shore A)
RC	10.0	268	62
R4	9.5	201	63
Q4	8.9	188	67
S4	8.6	215	68

shapes and dimensions.³¹ The mismatch in surface energy between plastic and rubber components at the interface may result in uneven flow during processing. Incompatibilities also extend to thermal properties, causing differential shrinkage and warping during temperature variations. Chemical incompatibility may lead to reactions between components, resulting in material degradation, embrittlement or discoloration. Various strategies exist to enhance compatibility between rubber and plastic in TPEs,

including the use of appropriate compatibilisers, appropriate formulation design and advanced processing techniques. Surface modification is another method to address incompatibility issues effectively.³² A comprehensive understanding and resolution of incompatibility are crucial for optimising TPE performance and ensuring the quality of end products. Tailoring TPEs to specific applications relies heavily on achieving compatibility between plastic and rubber components.

Thermal stability of selected rubber compounds

TGA is employed to measure the mass change of a material as its temperature increases, while the derivative DTGA (DTGA) provides insights into the rate of this mass change with temperature. Figures 2 to 5 depict TGA and DTGA graphs for the reference compound (RC), and compounds R4, Q4 and S4, each containing 25 phr of plastics (PVC, PET and a blend of PVC–PET) in formulations (Table 1), respectively. Figure 2 illustrates a 5% mass loss occurring between 141°C and 320°C, attributed to light, non-polymeric materials in the compound's formulation. The corresponding DTGA curve indicates a relatively low reaction rate during this mass loss. Subsequently, IIR degradation initiates from 320°C, continuing until 444 °C with a total mass loss of 84%, exhibiting a higher reaction rate. This increased degradation temperature range, compared to gum or uncured IIR (typically 180°C–250°C,^{13,14} results from crosslinking (curing) of gum IIR rubber with the studied formulation. In Figure 3, three distinct mass loss regions, 172°C to 273°C, 288°C to 321°C, and 322°C to 418°C with 16%, 2% and 64% mass losses are observed for compound R4 with 25 phr PVC. The first region involves the degradation of non-polymeric materials and the initial dehydrochlorination of PVC, exhibiting a low reaction rate. The second area indicates the continuation of PVC dehydrochlorination. The third area, characterised by a high reaction rate, corresponds to the overlapping degradation of IIR and significant dehydrochlorination of PVC. Figure 4 presents three mass loss regions 153°C to 235°C, 267°C to 440°C and 443°C to 496°C with 0.3%, 84%, and 2% mass losses, respectively, for compound Q4 with 25 phr PET. The first region, exhibiting a low reaction rate, is attributed to the degradation of non-polymeric materials. The second region indicates the degradation of IIR and depolymerisation of PET, with a high reaction rate. The third region corresponds to the final depolymerisation of PET, demonstrating a low reaction rate. Figure 5 displays four mass loss regions 159°C to 264°C, 272°C to 326°C, 326°C to 438°C and 438°C to 522°C with 7%, 7%, 70% and 6% mass losses for compound S4 with 25 phr PVC–PET (50–50). The first and last regions involve the degradation of light non-polymeric materials and the final depolymerisation of PET, respectively. The middle two regions, characterised by high reaction rates, correspond to the degradation of IIR, dehydrochlorination of PVC and the primary depolymerisation of PET, with some overlap. The presence of PVC, PET and IIR in the TPE formulation results in multilateral

interactions, causing a shift in degradation temperatures based on the type and amount of each plastic component. It was concluded that the presence of PVC, PET and IIR in the TPE influences thermal stability and degradation behaviour. Also, the type and amount of each plastic impact the degradation temperature and rate. Overlapping mass loss peaks in TGA curves indicated simultaneous degradation of different components, while PVC showed dehydrochlorination peaks, PET exhibited peaks for depolymerisation. Curing and also combining plastics with IIR altered the initial degradation temperature of IIR compared to its uncured state. This analysis provided valuable insights into the thermal behaviour of the different TPE formulations. By understanding the interaction and degradation profiles of each individual component, researchers can optimise TPE formulations for specific applications and requirements.

The curing properties of studied rubber (TPE) compounds

Table 2 presents crucial curing parameters, including scorch time (t_{s2}), optimum cure time (t_{90}), Δ torque and CRI for the examined rubber (TPE) compounds. The scorch time for the RC compound was 4 minutes and 40 seconds. Incorporating PVC in the rubber compound resulted in an increase in this parameter, from 5 minutes and 9 seconds for compound R0 to 6 minutes and 32 seconds for compound R4 with 25 phr PVC. However, the addition of PET had a negligible effect on scorch time, with minimal change observed. The reasons may refer to two major issues, immiscibility and limited interfacial area between IIR and PET in the blend. PET and IIR might be immiscible, meaning they don't interact well on a molecular level. This could prevent PET from interfering with the crosslinking reactions in IIR during curing, leading to minimal impact on scorch time. Also, if the PET was dispersed as large particles within the IIR matrix, the interfacial area between the two polymers might be minimal. This would limit the potential for PET to physically hinder the crosslinking process in IIR. The introduction of a PVC–PET (50–50) blend initially increased the scorch time to 5 minutes and 55 seconds, but further additions of the plastic blend showed no significant impact on this parameter. The optimum cure time for the reference compound (RC) without plastic in the formulation was 10 minutes and 24 seconds, which increased to 12 minutes and 34 seconds for compound R4. An increase in PVC content in the TPE formulation resulted in an extended optimum cure time. Surprisingly, the incorporation of PET had an adverse effect on this parameter, reducing it to 8 minutes and 39 seconds for compound Q4 with 25 phr PET. The optimum cure time for compounds S0 to S4 with a blend of PVC–PET remained relatively unchanged. Δ torque showed minor changes with the incorporation of plastic in the TPE composition, increasing from an initial value of 3.4 dN.m for RC to 3.7 dN.m for R4. However, the presence of PET had a more pronounced effect, raising

Δ torque to 4.9 dN.m for compound Q4. For the PVC–PET blend, no consistent trend was observed, and Δ torque generally increased with the plastic content in the TPE. The CRI, indicating the cure rate of a rubber compound, was 0.30 (1/second) for the IIR rubber compound without plastic in the formulation. This parameter exhibited limited fluctuation based on the plastic content in the TPE formulation, without following a regular trend. Overall, the studied plastics had little effect on the crosslinking of IIR but influenced pre-scorch risk. Additionally, the optimum cure times for PVC and PET increased and decreased, respectively. These results underscore the intricate interactions between various plastics and IIR in TPEs, emphasising the need for care consideration when optimising formulations to achieve desired effects on scorch time, optimum cure time, Δ torque and CRI.

The resistance to swelling, CLD and mechanical properties of studied rubber (TPE) compounds

As previously mentioned, IIR exhibits limited resistance to oils, organic solvents and strong oxidising agents. This limitation served as a significant motivation to incorporate the studied plastics into the formulation of IIR rubber compounds. The utilisation of a toluene swelling test, a well-established and widely employed method, allows for the measurement of butyl rubber resistance against organic solvents.³³ The swelling index is determined using the formula: (Swollen weight – Initial weight) / Initial weight multiplied by 100. A higher swelling index indicates lower resistance to organic solvents. Figure 6 presents a comparison of the swelling indexes of IIR–PVC, IIR–PET and IIR–PVC–PET prepared TPEs with varying amounts of plastics 5, 10, 15, 20 and 25 phr. The swelling index of RC (reference compound) without plastic in the formulation was 216%. The introduction of 5 phr PVC reduced it to 193%, and further additions of PVC resulted in values of 199%, 190%, 198% and 184%, all lower than the RC value (216%). Similar trends were observed for IIR–PET TPEs, consistently displaying lower values than RC: 170%, 169%, 202%, 186% and 164% for PET content of 5, 10, 15, 20 and 25 phr, respectively. The swelling indexes of TPEs containing the PVC–PET (50–50) plastic blend were lower but notably close to the RC value, ranging between 200% and 207%. These results highlight the positive impact of plastic incorporation on the organic solvent resistance of IIR-based TPEs. The observed phenomena can be attributed to several factors, categorised as follows:

- **Physical barrier effect:** Both PVC and PET contribute to the formation of a physical barrier that hinders the diffusion of toluene molecules into the butyl rubber matrix. This hindrance may result from their denser structure or interactions with the IIR chains, restricting the penetration of the solvent.
- **Crosslinking enhancement:** Plastics such as PVC and PET can serve as co-agents during crosslinking (refer

to Figure 7), promoting the development of a more densely linked network within the IIR compound. This compact network structure becomes less susceptible to solvent swelling. The CLD of the RC compound without plastic in the formulation was 113mol/m³, which generally and with few exceptions increased to higher values, as depicted in Figure 7.

- **Crystallinity increase:** The incorporation of PET may introduce crystallinity into the TPE, establishing crystalline domains that further impede solvent diffusion. This effect could elucidate the lower swelling index observed with PET compared to PVC.
- **Interfacial interactions:** Specific interactions occurring between plastic chains and IIR molecules at the interface may influence the solvent uptake behavior. These interactions could create a more ordered or impenetrable interface, resisting solvent penetration.
- **Synergistic effect of the blend:** The PVC–PET blend may exhibit a synergistic effect where the combined physical barrier and potential interfacial interactions of both plastics contribute to the observed decrease in the swelling index. However, this decrease remains closer to the reference compound compared to the individual additions of each plastic.

These insights provide a comprehensive understanding of how the interplay of physical, chemical and structural factors affects the organic solvent resistance of IIR-based TPEs, essential for optimising their formulations and applications.

Table 3 compares the crucial mechanical properties, tensile strength, elongation at break and hardness of IIR rubber compound (RC) and selected TPEs compounds, R4, Q4 and S4 with 25 phr PVC, PET and PVC–PET (50–50) blend in formulations, respectively. As observed, RC as a reference compound had 10 MPa, 268%, and 62 (Shore A), tensile strength, elongation at break and hardness, respectively. However, the tensile strengths for compounds R4, Q4 and S4 reduced to values of 9.5, 8.9 and 8.6 MPa, with the incorporation of PVC, PET and PVC–PET blend, respectively. Similar to tensile strength, the elongation at break for all TPEs was lower than the value for IIR rubber compound without plastics in formulation with the values of 201%, 188% and 215% for compounds R4, Q4 and S4, respectively. As expected, the incorporation of plastic in TPE had a positive effect on the hardness of the compounds, increasing it from 62 to the values of 63, 67 and 68 for compounds R4, Q4 and S4, respectively. The observed changes in tensile strength, elongation at break and hardness of TPEs compared to the reference IIR rubber compound (RC) can be attributed to several factors related to the incorporation of plastics PVC, PET and PVC–PET blend in TPE formulation. Incompatible interactions between IIR and plastics might lead to phase separation, creating weak boundaries within the material that can initiate fractures under stress and consequently reduction in tensile strength. Also, replacing some IIR chains with plastics, especially rigid PVC, can limit the material's ability to deform before breaking. In the case of PET, it can

introduce crystallinity in the TPE, causing stiffer and brittle regions that restrict overall deformation. All mentioned phenomena may reduce the elongation at the break of the TPE. It was concluded that PVC reduces tensile strength and elongation due to lower compatibility with IIR and phase separation while contributing more to hardness due to its rigid structure. PET may lead to slightly greater reductions in tensile strength and elongation compared to PVC due to it introduces crystallinity that further decreases elongation at break and tensile strength but increases hardness similarly to PVC. Also, the combined effects of both plastics in the blend (PVC–PET) influence the mechanical properties. Here, hardness benefits from both components. However, while plastics improve hardness, their incorporation generally comes at the expense of tensile strength and elongation at the break due to changes in crosslinking density, crystallinity and interfacial interactions. Choosing the type and amount of plastic depends on the desired balance between these mechanical properties and the intended application of the TPE.

The potential applications of produced TPEs depend on several factors, including:

- Success of compatibilisation: As discussed earlier, achieving a good blend with these materials can be challenging. If a compatible blend can be achieved, the properties can be tailored based on the ratio of each component.
- Final properties of the blend: The balance of elasticity (from IIR), strength (potentially from PET) and rigidity (potentially from PVC) will determine the suitability for specific applications.

However, based on observed results, they may use as gaskets, seals, chemical resistance hoses, protective coating, automotive parts and vibration damping components.

Conclusions

From this study, it was concluded that TPEs require compatibility between plastic and rubber components for optimal performance. Incompatibility can lead to blend heterogeneity, phase separation, poor adhesion and processing difficulties. The thermal stability of TPEs containing PVC, PET and IIR depends on the type and amount of each plastic. Each plastic influences degradation temperatures and rates through various interactions. PVC and PET impact the curing behaviour of IIR-based TPEs differently. PVC increases scorch time and optimum cure time, while PET reduces optimum cure time but has minimal effect on scorch time. The incorporation of PVC and PET improve the organic solvent resistance of IIR-based TPEs, likely due to physical barrier effects, enhanced crosslinking, increased crystallinity and specific interfacial interactions. Adding plastics to IIR generally reduces its tensile strength and elongation at break. This can be attributed to incompatible interactions, phase separation and increased crystallinity. Incorporating plastics increases the hardness of IIR-based TPEs. Their rigid structure and potential filler

effect contribute to this improvement. Choosing the type and amount of plastic in a TPE formulation involves balancing competing effects. Hardness typically increases, but tensile strength and elongation at break often decrease with higher plastic content. Understanding the interaction and degradation profiles of individual components in TPEs is crucial for optimising formulations for specific applications and requirements. Further research is needed to fully elucidate the complex interplay between plastics and IIR in TPEs and to develop advanced strategies for controlling compatibility and achieving desired properties. By carefully selecting and combining plastics with IIR, TPEs can be tailored for a wide range of applications requiring specific combinations of thermal stability, curing behaviour, solvent resistance and mechanical properties. The authors suggest to try Maleic anhydride grafted polymers (MA copolymers) and/or epoxy resins as compatibilisers for future study to improve studied properties of TPE.

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Author contributions

SMM and SOM designed the experiments. AS validated the data. SMM prepared the manuscript with contributions from all co-authors. The authors applied the SDC approach for the sequence of authors.

Data availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

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References

1. Costa FR, Dutta NK, Choudhury NR, et al. Thermoplastic elastomers. In: *Current topics in elastomers research*. Cleveland, OH, USA: CRC Press, 2008, pp.101–164.
2. Holden Geoffrey. Thermoplastic elastomers and their applications. In: *Applied polymer science: 21st century*. Amsterdam: Elsevier, 2000, pp.231–256.

3. Wang W, Lu W, Kang NG, et al. *Thermoplastic elastomers based on block, graft, and star copolymers*, vol. 7, p.1901679. Rijeka: InTech, 2017.
4. Basak S. Thermoplastic elastomers in biomedical industry—evolution and current trends. *J Macromol Sci Part A* 2021; 58: 579–593.
5. Ceseracciu L, Heredia-Guerrero JA, Dante S, et al. Robust and biodegradable elastomers based on corn starch and polydimethylsiloxane (PDMS). *ACS Appl Mater Interf* 2015; 7: 3742–3753.
6. Rahmany Naeim Abady A and Ostad Movahed S. The effect of curing system on the properties of the thermoplastic elastomer foams of ethylene-vinyl acetate copolymer and styrene-butadiene and ethylene-propylene-diene monomer rubbers. *J Appl Polymer Sci* 2017; 134: 45357.
7. Fang W, Fan X, Jiao H, et al. Characterization and properties of thermoplastic polyether elastomer/polyoxymethylene blends prepared by melt-mixing method. *Polymer Sci Series A* 2019; 61: 890–896.
8. Drupitha MP, Naskar K and Nando GB. Compatibilized TPU-PDMS blends: pros and cons of melt mixing and solution mixing techniques. *J Appl Polymer Sci* 2017; 134: 45164.
9. Guseynova ZN, Kahramanov NT, Hasanova AA, et al. Reactive extrusion of dynamic elastoplastics on the basis of thermoplastic polyolefins and butyl rubber. *Kimya Problemleri* 2019; 2: 267–274.
10. Jiang F, Wang Z, Qiao Y, et al. A novel architecture toward third-generation thermoplastic elastomers by a grafting strategy. *Macromolecules* 2013; 46: 4772–4780.
11. Koo JM, Kang J, Shin SH, et al. Biobased thermoplastic elastomer with seamless 3D-printability and superior mechanical properties empowered by in-situ polymerization in the presence of nanocellulose. *Compos Sci Technol* 2020; 185: 107885.
12. Chen Y, Wang W, Yuan D, et al. Bio-based PLA/NR-PMMA/NR ternary thermoplastic vulcanizates with balanced stiffness and toughness: “soft–hard” core–shell continuous rubber phase, in situ compatibilization, and properties. *ACS Sustain Chem Eng* 2018; 6: 6488–6496.
13. Khavarnia M and Movahed SO. Butyl rubber reclamation by combined microwave radiation and chemical reagents. *J Appl Polymer Sci* 2016; 133: 43363. doi:10.1002/app.43363
14. Miranian Z, Ostad Movahed S and Ostad Movahed N. The phenolic cured butyl rubber reclamation using different de-crosslinking agents. *Prog Rubber Plast Recycl Technol* 2023; 40: 14777606231186631.
15. Al Christopher C, da Silva ÍG, Pangilinan KD, et al. High performance polymers for oil and gas applications. *React Funct Polym* 2021; 162: 104878.
16. Tang S, Li J, Wang R, et al. Current trends in bio-based elastomer materials. *Sus Mat* 2022; 2: 2–33.
17. Lima R, Silva J, Vasconcelos M, et al. Bibliometric survey of the PVC production—part I: the continuous polymerization challenge. *Polimeros* 2023; 33: e20230013.
18. Khan SM, Gull N, Khan RU, et al. Polyvinylchloride (PVC): structure and properties relationship. In: *Polyvinylchloride-based blends: preparation, characterization and applications*. Bern, Switzerland: Springer, 2022, pp.19–47.
19. Nisticò R. Polyethylene terephthalate (PET) in the packaging industry. *Polymer Testing* 2020; 90: 106707.
20. Benyathiar P, Kumar P, Carpenter G, et al. Polyethylene terephthalate (PET) bottle-to-bottle recycling for the beverage industry. A review. *Polymers* 2022; 14: 2366.
21. Yao P, Wu H, Ning N, et al. Properties and unique morphological evolution of dynamically vulcanized bromo-isobutylene-isoprene rubber/polypropylene thermoplastic elastomer. *RSC Adv* 2016; 6: 11151–11160.
22. Yao P, Wu H, Ning N, et al. Microstructure and properties of bromo-isobutylene–isoprene rubber/polyamide 12 thermoplastic vulcanizate toward recyclable inner liners for green tires. *RSC Adv* 2016; 6: 30004–30013.
23. Tang Q, Hu S, Han L, et al. Morphological evolution and damping properties of dynamically vulcanized butyl rubber/polypropylene thermoplastic elastomers. *Polymers* 2022; 14: 2740.
24. Van Dyke JD, Gnatowski M, Koutsandreas A, et al. Effect of butyl rubber type on properties of polyamide and butyl rubber blends. *J Appl Polymer Sci* 2004; 93: 1423–1435.
25. Dutta NK and Tripathy DK. Influence of curing systems on the properties of bromobutyl rubber: part III—effect of different types of curing systems on the cure characteristics, physical properties and thermo-oxidative degradation characteristics. *Polymer Degrad Stability* 1992; 36: 73–80.
26. Goto SI, Kimura K, Yamamoto T, et al. A novel gas-barrier elastomer composed of butyl rubber and polyamide. *J Appl Polymer Sci* 1999; 74: 3548–3552.
27. Guseynova ZN, Kakhramanov NT, Mamedov BA, et al. Thermoelastoplastics based on a mixture of thermoplastic polyolefins and butyl rubber. *Inorganic Mater Appl Res* 2019; 10: 381–386.
28. Fazli A and Rodrigue D. Waste rubber recycling: a review on the evolution and properties of thermoplastic elastomers. *Materials* 2020; 13: 782.
29. Mohite AS, Rajpurkar YD and More AP. Bridging the gap between rubbers and plastics: a review on thermoplastic polyolefin elastomers. *Polymer Bull* 2022; 79: 1–35.
30. Panigrahi H, Sreenath PR and Kotnees DK. Unique compatibilized thermoplastic elastomer with high strength and remarkable ductility: effect of multiple point interactions within a rubber-plastic blend. *ACS Omega* 2020; 5: 12789–12808.
31. Liu S, Peng Z, Zhang Y, et al. Compatibilized thermoplastic elastomers based on highly filled polyethylene with ground tire rubber. *J Appl Polymer Sci* 2022; 139: e52999.
32. Coran AY. Thermoplastic elastomeric rubber-plastic blends. In: *Handbook of elastomers*. Cleveland, OH, USA: CRC Press, 2001.
33. Khalaf AI, Yehia AA, Ismail MN, et al. High performance oil resistant rubber. *Open J. Org. Polym. Mater.* 2012; 2: 88–93. doi:10.4236/ojpm.2012.24013