IIETA International Information and Engineering Technology Association
Advancing the World of Information and Engineering

Revue des Composites et des Matériaux Avancés-Journal of Composite and Advanced Materials
Vol. 34, No. 5, October, 2024, pp. 621-633
Journal homepage: http://iieta.org/journals/rcma

# Toughening of Epoxy Systems by Adding Three Toughness Modifiers as Quaternary Blends of Polymeric Materials

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https://doi.org/10.18280/rcma.340510

**Received:** 29 August 2024
**Revised:** 20 September 2024
**Accepted:** 29 September 2024
**Available online:** 31 October 2024

***Keywords:***
*epoxy resin, mechanical properties, toughness propertied, quaternary polymeric blends, toughened epoxy*

## ABSTRACT

Epoxy systems are widely used in high-performance applications due to their strong strength and high modulus of elasticity. However, their use in structural applications is limited by their low toughness and brittleness. This study aims to enhance the toughness of fragile epoxy resin by incorporating natural rubber (NR) and commercial plastics (PMMA and ABS). Two groups of polymeric blends were formulated: Epoxy/NR/ABS/PMMA. Ternary blends were prepared with varying weight percentages of NR and ABS, and the blend with 1% NR and 3% ABS showed the best tensile properties. Quaternary blends were then created by adding different percentages of PMMA to this ternary blend. The blend containing epoxy with 1% NR, 3% ABS, and 9% PMMA exhibited significant improvements in mechanical properties, including impact strength, flexural strength, fracture toughness, and tensile strength. Compared to neat epoxy and the ternary blend (1% NR: 3% ABS), the quaternary blend showed increases in flexural strength (42.7% and 23.1%, respectively) and flexural modulus (93.6% and 41.6%, respectively). The impact strength and fracture toughness of the quaternary blend improved by 82.2% and 115% over neat epoxy and by 47.2% and 44.46% over the ternary blend, respectively.

## 1. INTRODUCTION

Among the diverse range of polymeric materials employed as matrices in polymer composites, thermosetting materials and thermoplastics emerge as the primary categories. In various engineering applications, thermosetting polymers are extensively utilized due to their versatility, exceptional performance, high modulus and strength. In addition, their low viscosity allows for easy manufacturing at room temperature. Epoxy resins, in particular, are at the forefront of preferred thermosetting materials because of their pronounced features [1-3]. Epoxy resins offer significant advantages in engineering applications, attributed to several favorable characteristics. These include low shrinkage, increased rigidity, great chemical-based resistance, sound quality strength, excellent dimensional-based stability, and durable adhesion characteristics [4-6]. Despite the advantages epoxy offers, its inherent brittleness stems from a high crosslink density, low stress at fracture, frail impact strength, finite propagation of resistance to crack. Consequently, the inherent low toughness of epoxy resins poses significant constraints on their use in engineering applications [7]. One notable approach to enhance the toughness of epoxy involves introducing a second phase activated during the curing process, initiating toughening mechanisms when crack propagation occurs. Researchers have prioritized this strategy to improve epoxy properties. The resulting materials demonstrate low density, high stiffness, increased fracture toughness, and a favorable specific strength-to-weight ratio.

Over the last four decades, considerable research efforts have been dedicated to modifying epoxy resins to enhance these properties, and numerous reviews on this topic are available in the literature [8-12]. Improving the epoxy resins' toughness can be achieved via various approaches, including chemical modification, molecular weight increase, crosslink density adjustment, addition of reactive diluents, incorporation of toughness modifiers, and the introduction of inorganic fillers or reinforcements. Chemical modification involves altering the network structure to provide greater flexibility, while the distance between crosslinks can be enhanced through elevating the molecular weight of epoxy resin, hence increased toughness. Adjusting crosslink density by modifying the crosslinking agent to epoxy resin ratio is another effective approach. Additionally, the inclusion of reactive diluents in the formulation contributes to toughness improvement. Specific toughness modifiers can also be added to the resin formulation for enhanced performance. Lastly, the inorganic fillers and/or reinforcements incorporation into pristine resin further contributes to toughness enhancement [9, 13]. The improvement of ductility, fracture toughness, and tensile strength properties in the aforementioned resin is essential, and several modification methods are available to achieve these enhancements. Some of these techniques involve incorporating elastomeric materials to boost flexibility and impact resistance (elastomeric modification), introducing additional thermosetting components to alter curing behavior and overall properties (thermoset modification), and adding thermoplastic materials to enhance toughness and impact resistance, often through a two-phase system (thermoplastic modification). These approaches, among others, have been extensively researched and examined to customize and improve the performance of epoxy resin [14-18]. To improve the epoxy matrix system, synthetic rubber modifications can be made on the basis of epoxy monomer, by using soft rubber particles possessing different shapes. Many researchers have focused on the importance of applying these particles as reinforcing mechanism/s for fracture toughness increment [7, 9, 19-21]. The modification of epoxy resins involved incorporating various liquid modifiers, including natural rubber epoxidized [22], hydroxyl-terminated polybutadiene [23], and carboxyl groups terminated butadiene acrylonitrile rubbers [24]. Combining liquid rubbers with nanoparticles has been found to be of great potential as toughening epoxy resin technique. For more than 50 years, the enhancement of epoxy resin toughness using rubber has been acknowledged as one of the best methods for lessening brittleness and improving a variety of matrix characteristics. Liquid rubber-modified epoxy resins often exhibit increased flexibility and impact resistance. Many researchers have been interested in the integration of rubber along other possible nano-fillers, as this has demonstrated a significant advancement in both fracture toughness and ductility. Nevertheless, it is significant that this enhancement is accompanied by a drop in the cured polymers' hardness [25]. Rubber particles with low modulus typically led to a reduction in stiffness and thermal properties in polymer-based materials [26]. In an attempt to improve epoxy resins' characteristics, toughening agents such as hydroxyl-terminated polydimethylsiloxane has been used. This hydroxyl derivative is preferred because of its intrinsic properties, which include strong dielectric strength, good hydrophobicity, uniform physical features along an extensive temperature range, high thermal stability, efficient wetting, resistance to weather and ozone, a flexible molecular structure, and exceptional physiological inertness [27, 28]. Interest has grown in thermoset modification as a cost-effective and easily process able filler in epoxy, attributed to its high molecular weight properties. Several studies indicate that the fracture and mechanical features of epoxy resins experience enhancements because of the unsaturated polyester' low viscosity [29, 30]. Chozhan et al. [31] demonstrated a thorough investigation concerning the fracture toughness of epoxy resins where the incorporation of vinyl esters was examined. Higher loading content (5%, 10%, and 15% by weight) of vinyl ester oligomers resulted in improved mechanical characterization because of the complex cross-linked network formation.

The inclusion of thermoplastics in epoxy systems provides significant advantages, especially in terms of raised hardness and fracture toughness in comparison with many modifications of elastomers and thermoplastics, this is in contrast to cases during which there is a reduction in mechanical and thermal characterizations [32, 33]. Poly(acrylonitrile-co-butadiene-styrene) (ABS), Poly (ether ketone) (PEEK), Polycarbonate (PC), Polybutadiene (PB), Poly (aryl ether ketone), Poly(amide-ester), Poly (ether imide) (PEI), Polybutylene Terephthalate (PBT), and polysiloxanes are among the thermoplastics that are frequently used in this context. White and Sue [34] state that adding polyamide-12 (PA) particles can greatly improve the epoxy/MWCNT matrix's fracture toughness. They noted that the limitations on fracture toughness cannot be addressed by adding MWCNTs alone. Breakage toughness of an epoxy matrix could be suggestively increased through the addition of a thermoplastic filler. The ternary composite also exhibits noteworthy enhancements in strain at break and fracture toughness as a result of the filler phases' cooperative interaction.

Epoxy toughening has also been accomplished through the use of an engineering thermoplastic, so-called Poly(acrylonitrile-co-butadiene-co-styrene) (ABS). Numerous investigations on the mechanical and morphological behavior of epoxy/ABS hybrids were conducted. It is worth mentioning that the mechanical features of epoxy/ABS hybrids exhibit considerable enhancement at low contents of ABS and then reduce at relatively high loading, in contrast to epoxies toughened through alternative engineering thermoplastic/s [35, 36]. Mirmohseni and Zavareh [37] developed a more efficient technique for impact toughening epoxy. Their research demonstrated that the epoxy impact strength is greatly amplified when layered and particle nanofillers are added to ABS, a thermoplastic [37]. In 2015, Dobah et al. [38] looked into polyethylene addition effects on the impact and tensile features of reinforced epoxy using carbon fiber. The outcomes reveal that while all hybrid composites had improved tensile ductility, the lowest degree of polyethylene addition resulted in an augmented tensile strength. In contrast, the hybrid composites' impact characteristics declined as indicated by the Izod impact strength.

The composite material matrix was created using a modified epoxy resin, incorporating thermoplastic polymethylmethacrylate (PMMA) and polyacrylonitrile-co-butadiene (PACB) rubber. The results indicated enhancements in the composite's tensile and flexural strengths. Consequently, these high-strength, tough, and dimensionally stable composites are anticipated to significantly contribute to applications requiring high-performance structural properties [39]. Bakar et al. [40] reported an improved epoxy resins mechanical property via nanobent and PMMA addition. The composites with the most significant property improvements were those containing either 1% or 5% by weight of nanobent or modifier PMMA polymer. The hybrid nanocomposite with 1 weight percent nanobent and 5 weight percent PMMA exhibited a synergistic effect, as evidenced by increased flexural energy of fracture and bending stress at break. In contrast, epoxy nanocomposites based on 2% nanobent and 5% PMMA displayed brittle fracture energy compared to single-rate composites [40]. The effects of modified PMMA with halloysite nanoclay tubes (MHNTs) were investigated by Rudresh et al. [41]. The addressed research group then reported that the modification process produced a pliable interface that gave epoxy resin excellent ductility. As a result, the tensile strength and elongation at break were both significantly improved. In comparison to neat epoxy, values for thermal stability, fracture toughness, flexural modulus, flexural strength, and tensile modulus also exhibited notable improvements [41].

While epoxy resins are widely used in high-performance applications due to their excellent strength, high modulus, and chemical resistance, they suffer from significant limitations. The most critical of these is their inherent brittleness, which leads to low fracture toughness and poor impact resistance. These shortcomings make epoxy resins unsuitable for many structural applications, where materials are exposed to mechanical stresses, dynamic loading, and impact forces.

Furthermore, their ability to absorb energy before fracture is limited, causing premature failure in demanding environments. To overcome these limitations, epoxy resins often require modifications through the addition of toughening agents, which enhance their toughness without compromising their desirable properties. This study explores the use of NR, ABS, and PMMA to address these key challenges.

The ongoing research aims to enhance the ductility, fracture toughness, and tensile strength features of epoxy resin while minimizing brittleness. This objective is pursued by introducing ternary blends of Poly(acrylonitrile-co-butadiene-co-styrene) (ABS), polymeric materials—specifically, thermoplastic polymethyl methacrylate (PMMA), natural rubber (NR)—in various ratios into the epoxy resin. The study is dedicated to a comprehensive examination of essential mechanical properties within this context.

## 2. METHODOLOGY

### 2.1 Materials used

In this manuscript, utilized four distinct polymeric materials: epoxy resin, natural rubber (NR), poly(acrylonitrile-butadiene-co-styrene) (ABS), and polymethyl methacrylate (PMMA). The epoxy resin, specifically Euxit 50 KI, is a liquid resin with low-viscosity and a weight equivalent to epoxy of 185 eq/g. To transform it into a solid state, Hardener (Euxit 50 KII) was added with 1:3 ratio. The epoxy resin and the hardener were supplied by the Egyptian Swiss Chemical Industries Company. The project uses RSS-4 Grade Sheets of natural rubber, which are provided by North East India's Caoutchouc Horizon Company (ROMIL-SA select Assured solvent). The bulk NR was dissolved in toluene ($C_6H_5CH_3$). The Acrylonitrile Butadiene Styrene (ABS) utilized in the study was obtained in pellet form from Absolac (India), with dichloromethane serving as the solvent for ABS. Poly (methyl methacrylate) (PMMA) in white pellet form, with a product code GRM1746 and an average molecular weight of about 15,000, was supplied by HI Media Laboratories in India. Commercial-grade PMMA in granular form with transition temperature of 104°C, was acquired from an Indian chemical supplier located in Bangalore. The solvent used in PMMA, acetone ($(CH_3)_2CO$), was acquired via Kerala, India - Nice Chemicals (P) Ltd.

2.1.1 Preparation of pure epoxy resin

In the manufacturing process, steel molds with a thickness of 10 mm were produced to cast the samples, adhering to ASTM standards, and were grooved using a CNC milling machine. The inner cavities of these steel molds were coated with wax. Molds that had been prepared beforehand were filled with epoxy resin and the necessary quantity of hardener. For full curing, the epoxy resin molds were left to stand at room temperature for a full day. The ASTM-compliant, clean epoxy resin samples were removed from the molds. Before being put through mechanical testing, every sample was post-cured for four hours at 60 degrees Celsius in an oven to guarantee full curing. In each single instance, six specimens were created through which the mean value was recorded.

2.1.2 Formulation of ternary blends

To create blends of natural rubber (NR), acrylonitrile butadiene styrene (ABS), and epoxy resin, a similar methodology was employed. Blends of NR/ABS/epoxy were created by changing the epoxy's NR and ABS contents. Initially, the ABS pellets and natural rubber sheets were dissolved independently. One glass beaker was used to dissolve the natural rubber sheets in toluene, while another was used to dissolve the ABS pellets in dichloromethane. The procedure involved adding appropriate quantities of epoxy resin to a beaker, along with solutions of toluene containing NR and dichloromethane containing ABS in predetermined ratios. The blend consisted of varying percentages of NR (ranging from 0.5% to 1.5% by weight) and ABS (ranging from 1.5% to 4.5% by weight) in the epoxy resin. Following this, the epoxy/NR/ABS system underwent a degassing process and was subsequently cooled to room temperature. To remove toluene and dichloromethane, the mixture was heated to 110°C, ensuring complete evaporation. After achieving this, the blend of NR, ABS, and epoxy resin underwent continuous stirring at 100°C for one and a half hours, followed by cooling to room temperature. Next, hardener was added with thorough mix, after which the resultant mixture underwent another round of degassing. Before being poured into molds, the degassed resultant of epoxy, ABS, and NR were continuously stirred along the determined hardener amount. To ensure thorough and complete curing, the epoxy and hardener system underwent a 24-hour room temperature cure, after which a post-curing process was attained for 4-hour at 60°C.

2.1.3 Formulation of quaternary blends

Four polymer blend samples were prepared with a consistent composition of 1% natural rubber (NR) and 3% acrylonitrile butadiene styrene (ABS) by weight. These particular ratios were chosen based on the superior mechanical properties observed in the testing of triple polymer blend samples (epoxy: 1% NR: 3% ABS). The preparation process involved dissolving polymethyl methacrylate (PMMA) pellets in acetone ($(CH_3)_2CO$) within a glass beaker. Following this, a solution of toluene containing 1% NR and a solution of dichloromethane containing 3% ABS were meticulously combined with the acetone solution containing PMMA in the desired ratios. This mixture was then added to a beaker that contains the epoxy resin. The PMMA content in the epoxy resin blend was systematically varied, (3-12%) by weight. Following the established procedure for creating ternary blends, the quartet polymer blend underwent degassing and was allowed to cool down. Afterward, a specified quantity of hardener was introduced and mixed for ten minutes. The mixture underwent an additional round of degassing before being carefully poured into an ASTM-approved steel mold. The curing process mirrored the steps employed in the ternary polymer blend preparation, then the resulting product was subsequently subjected for mechanical testing.

### 2.2 Physical and mechanical characterization

The pre-defined tensile test specimen was prepared meticulously, adhering to a well-known standard (ASTM D 638) [42]. The evaluation of tensile properties utilized a WDW 200 E universal testing machine from China, with the test conducted at ambient temperature with speed of 5 mm/min foe the cross-head movement. For the assessment of bending behavior, the three-point test machine (China, WDW 200 E) was employed, following the specifications outlined in ASTM D-790-78 [43]. This test was carried out at room temperature with speed of 5 mm/min. The impact analysis was performed in accordance with ASTM ISO 179 [44] and took place at room temperature. The measurement test equipment for the Izod Charpy tension impact test was provided by New York, Inc., located in Amityville. Via dividing the absorbed impact energy recorded on cross-sectional area of the specimens', the impact strength ($kJ/m^2$) was computed. The TENSOR 27 model Fourier transform infrared spectrometer, made by the German company Bruker Optics Company, was utilized for Fourier Transform Infrared (FTIR) test, which followed the guidelines set forth by ASTM E1252 [45]. This spectrometer has a detector, so-called DTGS, operating at room temperature, a source of mid-IR that spans within the range of 400-4000 $cm^{-1}$ with KBr beams splitter. The surface topographies were investigated through Scanning Electron Microscope (SEM) technique using the Tescan VEGA-SB model from Belgium. To ensure optimal electrical conductivity, a gold sputtering process was applied to the surface along the edge of all samples. This combination of analytical techniques offers valuable insights into both the chemical composition (via FTIR) and the physical structure (via SEM) of the quartet polymer blend and neat epoxy samples.

## 3. RESULTS AND DISCUSSION

### 3.1 Fourier transform-infrared spectrometers (FTIR) test results

Improving a polymer matrix's performance attributes largely depends on the examination of the chemical and physical interactions between modifiers and epoxy resin. FTIR spectroscopy was utilized in this work to investigate possible bonding-based hydrogen between different polymeric modifiers and the epoxy resin [41]. Figure 1 illustrates the FTIR curve of neat epoxy resin as well as modified epoxy resin with different modifiers, including natural rubber (NR), and thermoplastic modifiers such as polyacrylonitrile-butadiene-co-styrene (ABS) and polymethyl methacrylate (PMMA). In Figure 1(a), the neat epoxy resin FT-IR spectra is presented within a frequency range of 400-4000 $cm^{-1}$ is presented, closely resembling spectra reported in the literature [40, 46, 47] and establishing a baseline for comparison. Subsequent figures in Figure 1 display FTIR spectra for modified epoxy resin using PMMA, natural rubber, and ABS providing a comprehensive characteristic of both neat epoxy resin as well as its modified counterparts. These analyses offer valuable insights into the molecular interactions contributing to the observed performance improvements in the polymer matrix. Three critical sites within the oxirane ring (epoxy groups) bands are thoroughly examined in order to characterize epoxy.

The methylene group C-H tension inside the epoxy ring is connected to first location, which can be found roughly at 3357 $cm^{-1}$. The epoxy group stretching vibration is represented by the second band at 914 $cm^{-1}$ and corresponds to the deformation of C-O within oxirane group (epoxide ring or –CH(O)CH–). Band detected at 1181 $cm^{-1}$ (third band), is ascribed to C–O stretching aromatic ring [46-48]. A wide-ranging band at 3357 $cm^{-1}$ is illustrated in Figures 1(a)-1(c), along with representative bands of the oxirane group. This broad absorption band, coupled with the oxirane group bands, is assigned to both aromatic and aliphatic –OH groups. These groups are acknowledged as the primary active functional groups and play a critical role in assessing hydrogen bonding, specifically in evaluating the quantity of hydroxyl groups present [49]. This meticulous analysis provides a comprehensive understanding of the functional groups within the epoxy resin and their potential contributions to molecular interactions and overall properties.

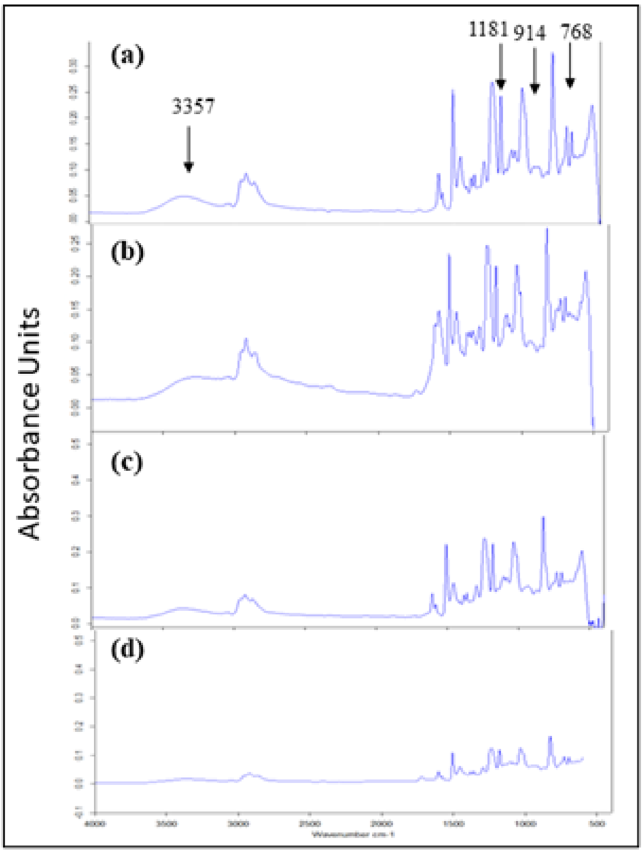

**Figure 1.** FTIR spectra for different formulations: (a) neat epoxy, (b) ternary polymeric blend (Epoxy:1%NR:3%ABS), and (c and d) quaternary polymeric blends (Epoxy:1%NR:3%ABS (9% or 12%) PMMA)

The infrared spectra elucidated in Figures 1(c)-1(d) for quaternary polymeric blends (Epoxy:1%NR:3%ABS:(9% or 12%) PMMA) after the curing process do not reveal any novel peaks or shifts in peak positions. Instead, there is a noticeable reduction in the intensity of the peak for all performance peaks.

A significant reduction is specifically observed at 3357 $cm^{-1}$, indicating –OH absorbance. This reduction becomes more prominent, particularly at higher PMMA contents in the blend, particularly at 12% by weight (Figure 1(d)) [50]. The decrease in peak intensity, particularly at 3357 $cm^{-1}$, implies a reduction in the concentration of hydroxyl groups. This reduction may be linked to an escalation in the cross-linking degree within the epoxy polymer blend [47]. Bakar et al. [40], gave different insights, though, by demonstrating that PMMA and individual amine moieties of the epoxy resin curing agent have particular interactions, while the polymer matrix with PMMA do not exhibit any discernible specific interactions. They suggested that the following reactions could explain the observed rise in OH group. First, OH groups with secondary amines are formed when a reaction is attained between the curing agent with the epoxy groups in the polymer matrix. The resultant compound then undergoes a reaction with PMMA's carbonyl groups, which creates hydrogen bonds. It is proposed that this interaction plays a main part in increasing the epoxy matrix toughness. These results highlight the intricate interactions within the epoxy polymer blend and imply that a variety of factors, such as hydrogen bonding and curing reactions, contribute to the materials' final features.

FTIR analysis showed reduced hydroxyl group concentrations, particularly with higher PMMA content, indicating increased cross-linking in the epoxy matrix. No new peaks were observed, but hydrogen bonding between the curing agent and PMMA was key to enhancing toughness. These interactions highlight the improved mechanical properties of the modified epoxy resin.

### 3.2 Mechanical test results

#### 3.2.1 Tensile test results

The tensile properties of two categories of polymeric blends, ternary and quaternary, both based on epoxy, are influenced by several factors. These include the kind and proportion of secondary materials in the blend, how evenly they are distributed, and how strong the bonds are at the blend constituents' interface. To delve into the mechanical behavior, specifically the stress-strain curves, of these polymer blends, tensile tests were conducted.

Figure 2 displays curves of stress-strain for ternary polymeric blends (Epoxy: X%NR: Y%ABS) as a subject to different weight ratios for each secondary material type. The weight ratios considered were (NR ratios (X) = 0, 0.5, 1, 1.5%wt.) and (ABS ratio (Y) = 0, 1.5, 3, 4.5%wt.) in the blend. The stress-strain curves depicted in Figure 2 highlight significant variations in behavior based on the type and weight ratios of secondary materials in the polymer blends. Notably, the curves demonstrate initial rigidity and brittleness for neat epoxy, transitioning to plastic deformation until fracture upon the addition of both acrylonitrile butadiene styrene (ABS) and natural rubber (NR) to the epoxy resin.

The curves further reveal that the specific blend composition involving 1%wt. natural rubber (NR) and 3%wt. acrylonitrile butadiene styrene (ABS) yields higher tensile strength compared to other ratios of NR and ABS in the polymer blend. This indicates that the precise combination of 1%wt. NR and 3%wt. ABS significantly contributes to the improved tensile strength. These observations emphasize the nuanced influence of secondary materials with their proportions on the mechanical characteristics of the polymer blends, offering valuable insights for optimizing the blend composition to enhance overall performance.

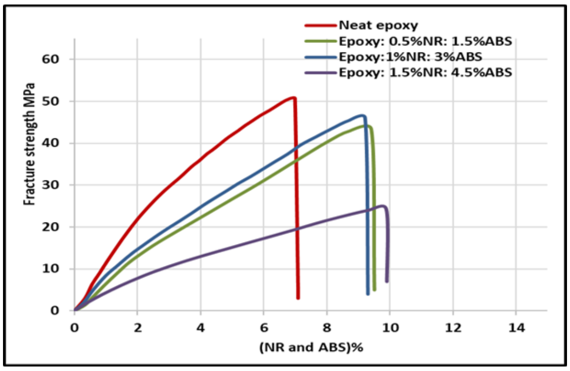

**Figure 2.** The stress-strain curves for both neat epoxy and ternary polymer blends, denoted as (Epoxy: X%NR: Y%ABS), where the weight ratios considered were (NR ratios (X) = 0, 0.5, 1, 1.5%wt.) and (ABS ratios (Y) = 0, 1.5, 3, 4.5%wt.) in the blend

The Figures 3(a)-3(c) illustrate the tensile characteristics, such as elongation at break, modulus of elasticity, and tensile strength for both pure epoxy and ternary polymer blends (Epoxy: X%NR: Y%ABS). The Standard deviations are represented by error bars. Notably, the sample with the ratio (Epoxy: 1%NR: 3%ABS) demonstrates the highest stress and the lowest elongation at break compared to other ratios, with a stress of 46 MPa, elongation of 9.21%, and modulus of elasticity of 0.864GPa. Conversely, increasing NR to 1.5% and ABS to 4.5% results in reduced tensile properties, as shown in Figures 3(a)-3(c) and summarized in Table 1. This data elucidates how altering ternary polymer blend compositions impacts mechanical properties, highlighting the need for precise ratio selection to achieve desired performance. For instance, the (Epoxy: 1.5%NR: 4.5%ABS) ratio exhibits lower stress and higher elongation (24.3 MPa, 9.88%, 0.34GPa). The flexibility introduced by natural rubber (NR) and acrylonitrile butadiene styrene (ABS) chains mitigates the inherent brittleness of neat epoxy [40, 51]. Previous studies indicate that specific NR and ABS ratios enhance compatibility and reduce brittleness, emphasizing the importance of tailored polymer blend compositions for optimal mechanical properties [51-54].

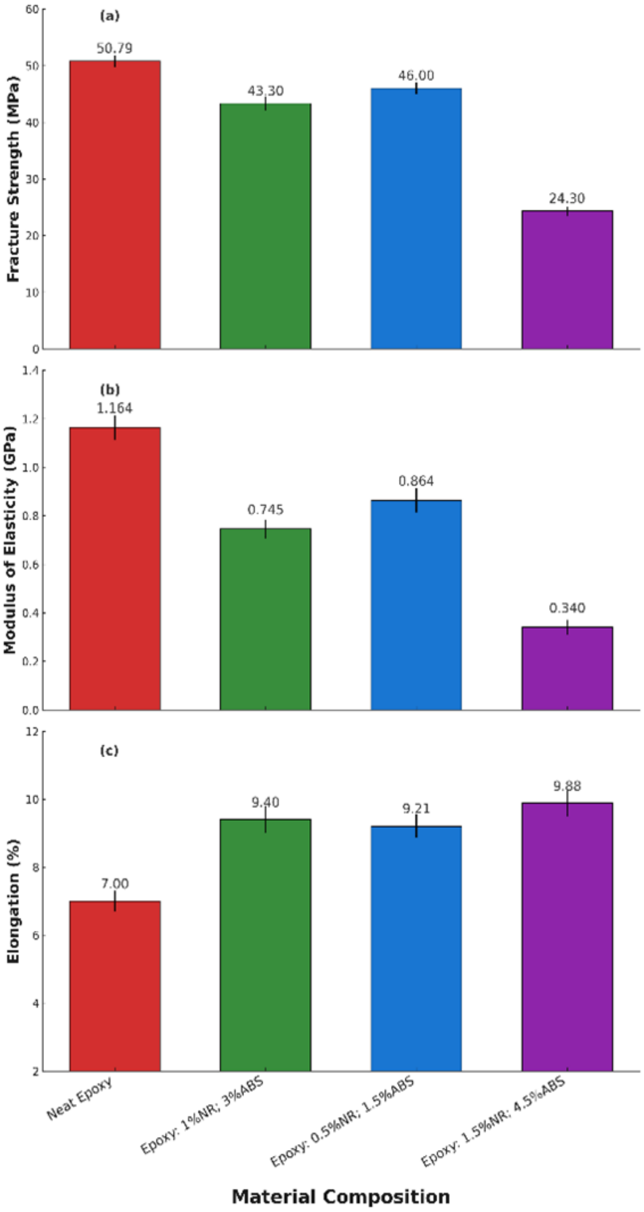

**Figure 3.** The tensile characteristics of both neat epoxy and ternary polymer blends (Epoxy: X%NR: Y%ABS) are presented. Error bars in the figures indicate the standard deviation. The properties include (a) tensile strength, (b) modulus of elasticity, and (c) percentage elongation at break

**Table 1.** Tensile properties of neat epoxy and ternary polymer blends (Epoxy: NR: ABS)

| Sample Composition | Fracture Strength (MPa) | Modulus of Elasticity (GPa) | Elongation (%) |
|---|---|---|---|
| Neat Epoxy | 50.79 | 1.164 | 7 |
| Epoxy: 0.5% NR: 1.5% ABS | 43.3 | 0.745 | 9.4 |
| Epoxy: 1% NR: 3% ABS | 46 | 0.864 | 9.21 |
| Epoxy: 1.5% NR: 4.5% ABS | 24.3 | 0.34 | 9.88 |

The paragraph discusses a sequential exploration of polymer blends, initiated by selecting an optimal ternary polymer blend, denoted as (Epoxy: 1%NR: 3%ABS), based on superior tensile strength from earlier results. This chosen ternary blend underwent further modification by introducing polymethyl methacrylate (PMMA) to form quaternary polymeric blends. Subsequently, mechanical tests were applied to examine the characteristics and performance of the prepared quaternary blends systematically. This systematic approach built upon the favorable attributes observed in the selected ternary blend. Figure 4 visually depicts the impact of varying proportions of polymethyl methacrylate (PMMA) (3%, 6%, 9%, and 12%wt.) on stress-strain curves and tensile strength in quaternary polymeric blends ((Epoxy: 1%NR: 3%ABS): X%PMMA). Notably, the figure indicates a transformation in the tensile behavior of quaternary blends. It transitions from the initially observed soft and tough behavior in the ternary blend (Epoxy: 1%NR: 3%ABS) to a stronger and tougher behavior upon adding the PMMA to the ternary blends. This shift aligns with the inherent flexibility of the polymeric chains in PMMA and ABS compared to the rigid chains in neat epoxy [41, 55]. The results suggest that introducing PMMA contributes to enhancing the overall strength and toughness of the polymer blend, highlighting the substantial impact of meticulous composition adjustments on the mechanical features of quaternary polymeric blends.

Elongation at break of neat epoxy, modulus of elasticity, tensile strength, and quaternary polymer blends based on epoxy (epoxy: 1%NR: 3%ABS: X%PMMA) are displayed in Figures 5(a)-5(c) and summarized in Table 2.

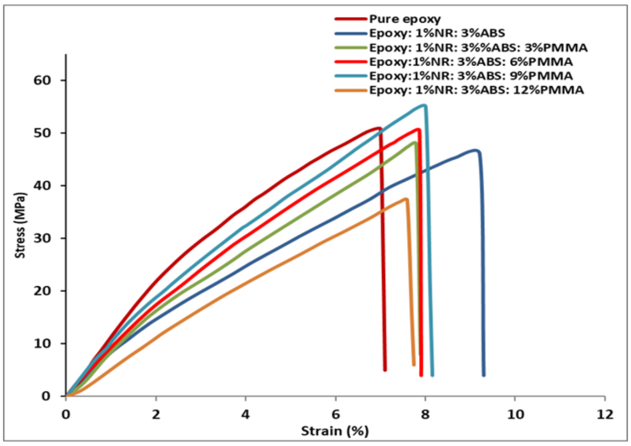

**Figure 4.** The stress–strain curves are presented for neat epoxy, a ternary polymeric blend (Epoxy: 1%NR: 3%ABS), and various quaternary polymeric blends ((Epoxy: 1%NR: 3%ABS): X%PMMA) with different ratios of PMMA (3%, 6%, 9%, and 12%wt.) in the blend

Standard deviation is represented by error bars in the figure. As shown in Figure 5(a), the PMMA addition to the ternary polymer blend (Epoxy: 1%NR: 3%ABS) significantly increases the samples' fracture strength. When 9%wt. of PMMA is added to the ternary blend, the maximum values are seen. The structural properties of PMMA chains and the natural interfaces and interactions between the polymer blend's constituent parts are credited with this improvement. PMMA is added to the polymer blend as agent that promotes effective compatibility and interfacial reactions between the various phases ((Epoxy: 1%NR: 3%ABS): X%PMMA) [41]. The enhancement in modulus and tensile strength, along with the retention of ductility, signifies the reinforcing impact of PMMA, complemented by the ductility improvement facilitated by NR and ABS. These dual functions operate synergistically within the quaternary polymer blends [54]. The observed advancements in properties can be attributed to specific interactions among the modified polymeric materials (NR, ABS, and PMMA) and the epoxy matrix [56]. This collaboration between components contributes to an overall enhancement in the performance of the quaternary polymer blends. Correspondingly positive outcomes were reported by Rudresh et al. [41], employing a similar blending procedure, resulting in heightened Young's modulus and tensile strength in hybrid epoxy nanocomposites incorporating PMMA (6 wt.%). These findings underscore the influence of PMMA incorporation in fortifying quaternary polymer blends, underscoring the significance of meticulous composition adjustments in tailoring the mechanical properties of these blends for specific applications.

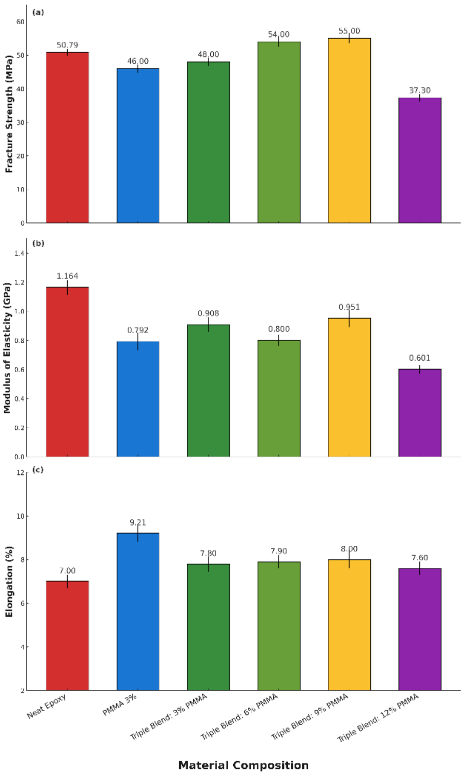

**Figure 5.** The tensile properties, including tensile strength (a), modulus of elasticity (b), and percentage elongation at break (c), are illustrated. Error bars in the figure represent the standard deviation. The data pertains to pure epoxy, ternary polymer blends (Epoxy: 1%NR: 3%ABS), and quaternary polymer blends ((Epoxy: 1%NR: 3%ABS): X%PMMA), showcasing different ratios of PMMA (3%, 6%, 9%, and 12%wt.) in the blend

**Table 2.** Tensile properties of neat epoxy and quaternary blends (Epoxy: NR: ABS: PMMA)

| Sample Composition | Fracture Strength (MPa) | Modulus of Elasticity (GPa) | Elongation (%) |
|---|---|---|---|
| Neat Epoxy | 50.79 | 1.164 | 7 |
| Epoxy: 1% NR: 3% ABS: | 46 | 0.792 | 9.21 |
| Epoxy: 1% NR: 3% ABS: 3% PMMA | 48 | 0.908 | 7.8 |
| Epoxy: 1% NR: 3% ABS: 6% PMMA | 51 | 0.8 | 7.9 |
| Epoxy: 1% NR: 3% ABS: 9% PMMA | 55 | 0.961 | 8 |
| Epoxy: 1% NR: 3% ABS: 12% PMMA | 37.3 | 0.601 | 7.6 |

Tensile tests revealed that adding NR, ABS, and PMMA significantly improved mechanical properties. The optimal ternary blend (1% NR, 3% ABS) showed higher tensile strength (46 MPa), while the quaternary blend with 9% PMMA achieved the highest strength (55 MPa) and modulus. These improvements are due to effective interactions between the modifiers and the epoxy matrix.

### 3.2.2 Flexural test results

Flexural strength is a critical indicator for the mechanical features evaluation of epoxy-based quaternary polymeric blends. Figures 6(a)-6(b) present the flexural characteristics, including flexural modulus and flexural strength, for both neat epoxy and quaternary polymer blends (Epoxy: 1%NR: 3%ABS: X%PMMA). Error bars in the figures designate the standard deviation. The flexural modulus and strength exhibit an increasing trend with the addition of PMMA, reaching a peak at 9 weight percent. Beyond this point, the increasing trend plateaus. In Figure 6(a), the quaternary polymeric blend with the composition Epoxy: 1%NR: 3%ABS: 9% PMMA demonstrates flexural strength values that surpass those of neat epoxy by 42.7% and exceed the ternary polymeric blend (Epoxy: 1%NR: 3%ABS) by 23.1%. Figure 6(b) reveals a similar pattern for flexural modulus, with increases of 48.8%, 75%, 93.6%, and 76.1% compared to neat epoxy when 3, 6, 9, and 12 wt.% of PMMA is incorporated into the ternary polymeric blend, respectively. Furthermore, the flexural modulus experiences increment of 9%, 28%, 41.6%, and 29%, respectively, compared to the sole ternary polymer blend (Epoxy: 1%NR: 3%ABS). This suggests that the inclusion of PMMA contributes to an improved flexural modulus in the quaternary polymeric blends. The introduction of PMMA, with its flexible chain structure, is believed to mitigate the epoxy chain rigidity, resulting in a decrease in flexural strength. Conversely, the abundance of PMMA-based active hydroxyl groups is thought to enhance density of cross-linking, thereby improving the mechanical behavior of the quaternary polymer blend [40, 41]. This delicate balance between structural and chemical interactions underscores the intricate interplay of components in influencing the flexural behavior of the polymer blend. Table 3 presents the flexural properties of both neat epoxy and the quaternary blends with NR, ABS, and PMMA.

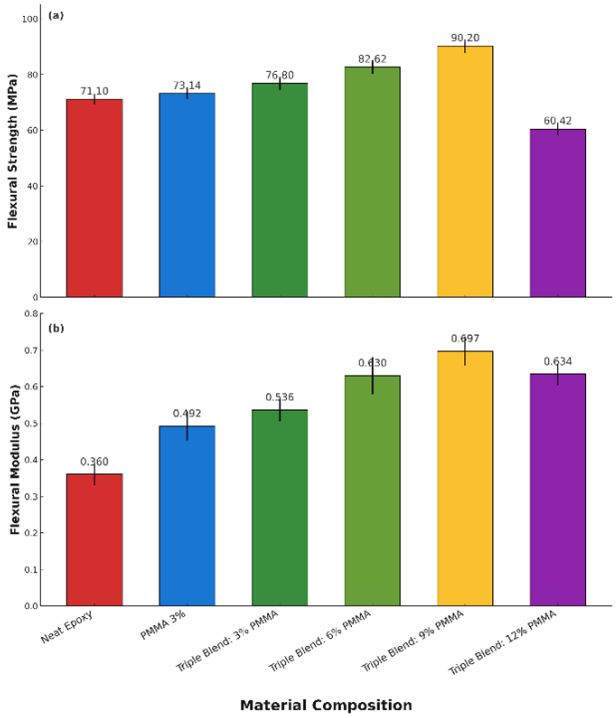

**Figure 6.** The flexural strength properties are depicted with error bars representing the standard deviation for pure epoxy, ternary polymer blends (Epoxy: 1%NR: 3%ABS), and quaternary polymeric blends ((Epoxy: 1%NR: 3%ABS): X%PMMA), featuring various PMMA ratios (3%, 6%, 9%, and 12%) in the blend. (a) Flexural strength and (b) Flexural modulus

**Table 3.** Flexural properties of neat epoxy and quaternary blends (Epoxy: NR: ABS: PMMA)

| Sample Composition | Flexural Strength (MPa) | Flexural Modulus (GPa) |
|---|---|---|
| Neat Epoxy | 71.1 | 0.36 |
| Epoxy: 1% NR: 3% ABS: | 73.14 | 0.492 |
| Epoxy: 1% NR: 3% ABS: 3% PMMA | 76.8 | 0.536 |
| Epoxy: 1% NR: 3% ABS: 6% PMMA | 82.62 | 0.63 |
| Epoxy: 1% NR: 3% ABS: 9% PMMA | 90.2 | 0.697 |
| Epoxy: 1% NR: 3% ABS: 12% PMMA | 60.42 | 0.634 |

The trend perceived in quaternary polymeric blend aligns with findings in other mechanical properties, showcasing higher values as compared with both ternary blend (Epoxy: 1%NR: 3%ABS) and neat epoxy systems. Likewise, impact strength and fracture toughness exhibit an increase with the addition of PMMA, peaking at 9 wt.% PMMA and plateauing in the trend when exceeding 9 wt.% PMMA as evidenced in Figure 7. Specifically, the impact strength and fracture toughness of the quaternary blend with the composition (Epoxy: 1% NR: 3%ABS: 9% PMMA) saw a remarkable increase of approximately 82.2% and 115%, respectively, in contrast to neat epoxy. Furthermore, they increased by around 47.2% and 44.46%, respectively, when compared to the ternary polymeric blend. This improvement is likely attributed to the synergistic effects arising from the combination of three distinct polymers (NR, ABS, and PMMA) acting as toughness materials, ultimately enhancing the overall impact resistance and fracture toughness of the quaternary polymeric blend. Incorporating plasticizers, such as thermoplastics or rubber, into epoxy thermosetting materials is a recognized and effective strategy for enhancing toughness.

The addition of NR, ABS, and PMMA significantly enhances the toughness of the epoxy matrix. Compared to other toughening agents like CTBN [57], nanoclays [58], and PES [59], our blend shows higher impact strength and fracture toughness without compromising stiffness or processing ease. Nanoclays improve toughness but face dispersion challenges, while PES increases fracture toughness at the cost of processing complexity. In contrast, our NR/ABS/PMMA blend offers a balanced solution with improved toughness, better compatibility, and cost-effective processing.

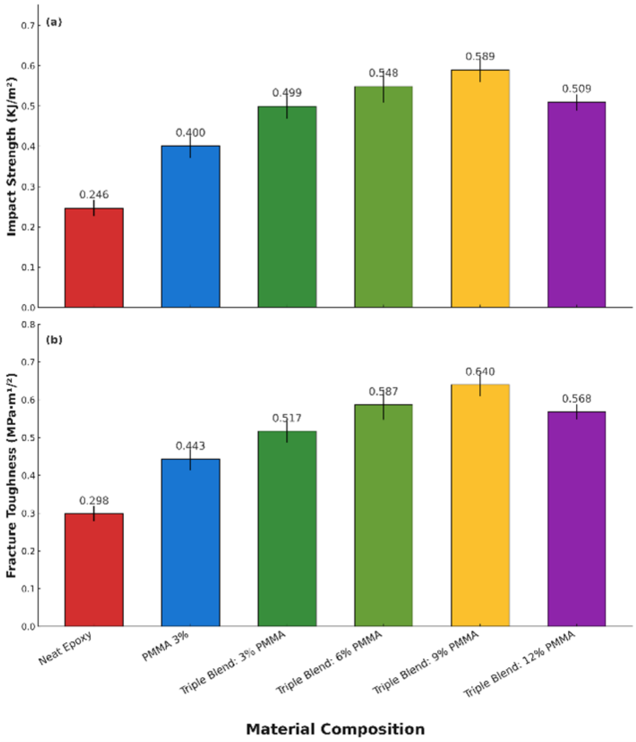

**Figure 7.** The fracture toughness properties are illustrated with error bars representing the standard deviation for pure epoxy, ternary polymer blends (Epoxy: 1%NR: 3%ABS), and quaternary polymeric blends ((Epoxy: 1%NR: 3%ABS): X%PMMA), featuring different ratios of PMMA (3%, 6%, 9%, and 12%) in the blend. The figure is divided into two subplots: (a) Impact strength and (b) Fracture toughness

The observed improvements in mechanical properties are a result of several toughening mechanisms activated by the addition of NR, ABS, and PMMA. Firstly, the phase separation morphology formed by NR and ABS within the epoxy matrix plays a crucial role in enhancing toughness by creating a secondary phase that dissipates energy during mechanical deformation. Crack pinning and crack deflection mechanisms also contribute to the higher impact strength and fracture toughness observed in the quaternary blends. Additionally, PMMA enhances the interfacial adhesion between the polymeric phases, allowing for better stress transfer, thus improving the tensile and flexural properties. This synergistic interaction between NR, ABS, and PMMA is crucial for the overall improvement in the toughness of the epoxy resin.

This method improves the final network flexibility through an introduction of second dispersed phase [13, 54, 60, 61]. However, as evidenced in the present study, when the PMMA content surpasses 9% by weight in the blend (reaching 12% PMMA), there is a reduction in both fracture toughness and impact strength of the quaternary blend. Despite this decrease, the properties still surpass those observed in the ternary blend and neat epoxy. The decline in fracture toughness and impact strength at higher PMMA content is because of the low relative compatibility between the epoxy matrix and the additives, resulting in the accumulation of additive particles. A more detailed understanding of this phenomenon will be provided in the subsequent discussion of the fracture morphology results obtained through scanning electron microscopy (SEM).

Table 4 displays the fracture toughness properties of both neat epoxy and the quaternary blends with NR, ABS, and PMMA.

**Table 4.** Impact strength and fracture toughness of neat epoxy and quaternary blends (Epoxy: NR: ABS: PMMA)

| Sample Composition | Impact Strength ($KJ/m^2$) | Fracture Toughness $(MPa)^{1/2}$ |
|---|---|---|
| Neat Epoxy | 0.246 | 0.298 |
| Epoxy: 1% NR: 3% ABS: | 0.4 | 0.443 |
| Epoxy: 1% NR: 3% ABS: 3% PMMA | 0.499 | 0.517 |
| Epoxy: 1% NR: 3% ABS: 6% PMMA | 0.548 | 0.587 |
| Epoxy: 1% NR: 3% ABS: 9% PMMA | 0.589 | 0.64 |
| Epoxy: 1% NR: 3% ABS: 12% PMMA | 0.509 | 0.568 |

The addition of NR, ABS, and PMMA significantly improved the flexural strength, impact strength, and fracture toughness of epoxy blends. The optimal blend (1% NR, 3% ABS, 9% PMMA) increased flexural strength by 42.7%, impact strength by 82.2%, and fracture toughness by 115% compared to neat epoxy. PMMA levels above 9% reduced performance due to compatibility issues, though values remained higher than the ternary blend. These improvements result from phase separation, crack pinning, and better interfacial adhesion.

### 3.3 Morphology test results

The examination of fracture morphology through scanning electron microscopy (SEM) is instrumental in comprehending the connection between mechanical properties and internal structure in polymeric blended systems. As emphasized in the literature, factors like thermoplastic end group functionality, molecular weight, and thermoplastic ratio may can affect the morphology of epoxy/thermoplastic in diverse conducts [62-64]. The SEM topographies illustrating the fracture surface morphology for neat epoxy, ternary polymer blend (Epoxy: 1%NR: 3%ABS), and quaternary polymer blends (Epoxy: 1%NR: 3%ABS: 9 and 12%PMMA) are presented in Figures 8(a)-(d), respectively. The micrograph of neat epoxy (Figure 8(a)) displays the characteristic brittleness of a thermosetting polymer. The fracture surface exhibits strip-like patterns, relatively smooth and glassy, devoid of obvious defects, highlighting its inherent hard and brittle nature. These findings are consistent with the measured low toughness of the material. As documented in numerous research studies, the fracture surface of glassy and brittle polymers typically exhibits a flat, smooth, and glassy appearance, indicative of low fracture energies [63, 65, 66]. Additionally, the SEM micrographs depict feather markings and crack forking, which are attributed to the associated energy as well as comparatively rapid crack advancement. The repeated multi-planar and forking nature attained serve as mechanisms to absorb the addressed energy in a highly brittle material [67].

In Figure 8(b), the micrograph illustrates the ternary polymer blend fractured surface with optimum composition ratios (Epoxy: 1%NR: 3%ABS). The incorporation of both NR and ABS within the epoxy resin alters the ternary polymer blend structure, reducing the prominence of stripes and increasing surface roughness. Polymers with rough surfaces possess the capability to undergo plastic deformation [68]. The dispersion of NR and ABS micro-particles is identified as a contributing factor to high impact strength and crack arrest. Thus, both NR and ABS phases exhibited new surface features in the rich epoxy matrix. In accordance with the reposted literature, two main factors can perform critical roles in epoxy toughening: the morphology of a modifier in the matrix of epoxy and the interfacial interactions between the epoxy and modifier. The phase separation morphology of a modifier in the epoxy matrix is well-known to significantly influence toughening of epoxy via a number of mechanisms like microcracking, crack path deflection, particle bridging, and crack pinning [69]. This study places significant importance on the phase separation morphology of natural rubber (NR) and acrylonitrile butadiene styrene (ABS) in fine particles form within the matrix of epoxy, as observed through SEM studies—a crucial aspect of epoxy toughening. The SEM (Figure 8(b)) and FTIR (Figure 1(b)) studies reveal relatively strong interactions between the two phases, further contributing to the toughening of epoxy. These interactions, combined with the specific achieved morphology, play pivotal roles in enhancing the ternary polymer blend mechanical behavior [70-72].

The morphological changes induced by the addition of polymethyl methacrylate (PMMA) are evident in SEM images, showcasing a dependency on the interfacial interaction betwixt the matrix components. Figure 8(c), displaying the SEM image of the quaternary polymer blend with optimum composition ratios (Epoxy: 1%NR: 3%ABS: 9%PMMA), demonstrates increased roughness attributed to PMMA addition. The SEM image illustrates well-oriented interaction between the constituents and the epoxy resin matrix, particularly at 9% PMMA content, suggesting enhanced adhesion in quaternary polymer blends. This improved adhesion implies a higher energy requirement for material deformation, resulting in an augmented mechanical strength of the quaternary polymer blend materials (Epoxy: 1%NR: 3%ABS: 9%PMMA) [73]. The rough structure observed on the fractured surface is likely a result of the polymeric modifiers, which constitute the dispersed secondary phases (NR, ABS, and PMMA) in the modified epoxy resin blend. The tightens-based thermoplastic modifiers of epoxy resin has been extensively explored, with the generally established mechanism which involving the creation of a semi-Interpenetrating Polymer Networks (semi-IPN) structure, leading to increased ductility in the epoxy resin matrix [74, 75]. Alternatively, it has been postulated that thermoplastic particles create a second phase through mechanisms such as deflection and crack pinning, resulting in considerable plastic distortion of this phase [41].

The premise is that a well-distributed thermoplastic phase within a matrix of brittle epoxy prevents and/or slow fracture development within the matrix\modifier mix. Some studies promote a continuous morphology as more effecting technique for polymer blends [75-81]. In this morphology, the attained surfaces are particularly rough, with striated unceasing phases and vast smooth patches related to plastic yielding inside the polymer matrix. In Figures 8(b)-(d), rough and striated regions are attributed to the thermoplastics (ABS and PMMA) phase, whereas the even regions are assigned to the epoxy-rich phase. Figure 8(c) micrograph is quite similar, superposed leaf-like structure, more elongated, and featuring a distinct in quaternary polymer blends. However, exceeding 9% PMMA content in the blend reduces compatibility with the epoxy, leading to the accumulation of additional particles (Figure 8(d)). Further increasing the PMMA ratio to 12% results in an even coarser fractured surface of the quaternary polymer blend.

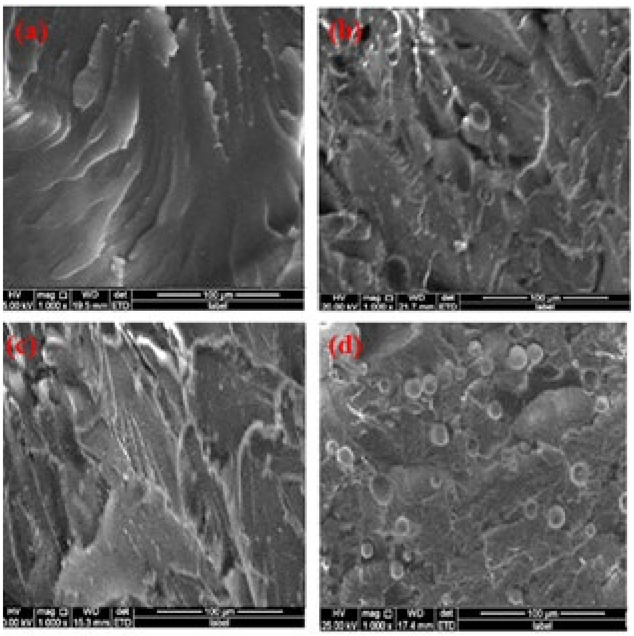

**Figure 8.** SEM images depict the fracture surface morphology at a magnification of X=1000 for pure epoxy, ternary polymer blends (Epoxy: 1%NR: 3%ABS), and quaternary polymeric blends ((Epoxy: 1%NR: 3%ABS): 9% and 12% PMMA)

SEM analysis showed that neat epoxy had a brittle, smooth surface, while the ternary blend (1% NR, 3% ABS) displayed increased roughness and crack resistance. Adding 9% PMMA further improved roughness and interfacial adhesion, enhancing strength. However, increasing PMMA to 12% reduced compatibility, leading to coarser fracture surfaces and decreased performance.

## 4. CONCLUSIONS

This study focuses on enhancing the toughness of epoxy resin by introducing three different polymeric materials as toughness modifiers. The addition of natural rubber (NR) and acrylonitrile butadiene styrene (ABS) to neat epoxy has delivered an improvement in the tensile behavior of the resulting ternary polymer blends based on epoxy. Building upon this observation, the ternary polymer blend (epoxy: 1%NR: 3%ABS) was chosen as the foundational blend for the preparation of quaternary polymeric blends, aiming to further increase the epoxy resin toughness. This modification strategy was applied to create additional polymeric blends with varying percentages of polymethyl methacrylate (PMMA) (epoxy: 1% NR: 3%ABS: X%PMMA).

The introduction of polymethyl methacrylate (PMMA) into the quaternary polymer blends, starting with the foundational blend (epoxy: 1%NR: 3%ABS), has resulted in a significant enhancement of mechanical properties. This improvement indicates effective interactions between the modifier components (NR, ABS, and PMMA) and the thermosetting epoxy matrix. In summary, the quaternary polymer blend with the component ratios (epoxy: 1%NR: 3%ABS: 9%PMMA) demonstrated superior mechanical properties, including fracture toughness, impact strength, flexural modulus, flexural strength, tensile modulus, and tensile strength. This outcome validates the success of the modification strategy in achieving overall enhanced mechanical performance in the quaternary polymer blend.

Notably, the fracture toughness and impact strength exhibited significant increases, approximately 115% and 82.2%, respectively, compared to neat epoxy. Similarly, they showed improvements of about 47.2% and 44.46%, respectively, compared to the ternary polymer blend. Examination through scanning electron microscopy (SEM) images presented favorable interactions between the epoxy resin and other modifier components (NR, ABS, and PMMA), particularly at the 9 wt.% PMMA composition. This observation indicates good adhesion and compatibility within the components of the quaternary polymer blend. However, an increase in PMMA content to 12 wt.% resulted in reduced compatibility, particle aggregation, and a rougher surface in the quaternary polymer blend. This suggests that there is an optimum PMMA content for achieving the desired properties, beyond which there is a decline in performance.

The study successfully demonstrated significant improvements in the toughness of epoxy resin by incorporating NR, ABS, and PMMA. These enhancements in tensile strength, flexural strength, and fracture toughness suggest that these modified epoxy systems could be suitable for industrial applications requiring high-performance materials, such as in aerospace, automotive, and construction industries. The increased toughness makes these materials particularly useful in structural applications that require both strength and durability.

However, certain limitations were encountered during the study. One limitation is the need for further optimization of PMMA content, as exceeding 9% led to diminished mechanical performance. Additionally, scaling up the production of these blends may pose challenges due to potential differences in curing dynamics and material distribution in large-scale processes. Future research should focus on addressing these limitations and exploring the long-term durability of these modified epoxy systems in industrial environments. In addition, further research is necessary to evaluate their long-term stability and performance under various environmental conditions, such as temperature changes, humidity, and UV exposure. This will be critical for assessing the durability and potential industrial applications of these epoxy systems. Moreover, from a sustainability perspective, NR is a renewable material derived from natural resources, offering an environmentally friendly aspect to the blend. However, ABS and PMMA are synthetic polymers, and their production and disposal may raise environmental concerns due to their non-biodegradable nature. Future research could focus on exploring greener alternatives to ABS and PMMA or developing recycling strategies to mitigate their environmental impact, making these toughened epoxy systems more sustainable.

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## NOMENCLATURE

| | |
|---|---|
| ABS | Acrylonitrile Butadiene Styrene |
| NR | Natural Rubber |
| PMMA | Polymethyl Methacrylate thermal |
| FTIR | Fourier Transform Infrared Spectroscopy |
| SEM | Scanning Electron Microscopy |
| Epoxy | Epoxy Resin |
| Tg | Glass Transition Temperature |

### Greek symbols

| | |
|---|---|
| $\alpha$ | Alpha, often used to represent thermal expansion coefficient |
| $\beta$ | Beta, used for various purposes such as strain or phase angle |
| $\varepsilon$ | Epsilon, strain |
| $\sigma$ | Sigma, stress |
| $\tau$ | Tau, shear stress |
| $\eta$ | Eta, viscosity |

### Subscripts

| | |
|---|---|
| c | Composite |
| f | Filler or fiber |
| m | Matrix |
| s | Sample or specimen |
| max | Maximum value |
| min | Minimum value |