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# Engineering properties of hybrid polymer composites produced with different unsaturated polyesters and hybrid epoxy

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ABSTRACT

In this study, the mechanical properties of hybrid polymer composites produced with different unsaturated polyesters and hybrid epoxy resins are investigated. The composites were produced by blending unsaturated polyester resins (i.e., orthophthalic, isophthalic, and terephthalic) and bisphenol-A-based epoxy-vinyl ester resin to produce single, binary and ternary blends. In doing this, a total of 14 different combinations were produced. The results show that the binary and ternary polymer blends tend to improve almost all the tested properties of the polymer composites. Further, the fourier-transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) results confirmed that the reason for enahcned properties is due to better crosslinking and longer chains of polymers produced in binary and ternary mixtures. The absence of peaks determining the styrene polymerization character for all mixtures also demonstrates that the polymerization reaction takes place in all mixtures. It is also believed that the binary and ternary resin mixtures have developed higher energy absorption compared to single resin composites. All of the mentioned has been achieved while the gelation temperatures of the hybrid resin mixtures were not changed significantly and they began gelation at the expected temperature values. In addition to the gelation, peak exotherm temperatures, and barcol hardness values demonstrated that all mixtures achieved sufficient curing. The result of this study is significant and point to the great potential of producing high performance polymer composites through the use of binary or ternary resin mixtures.

## 1. Introduction

Polymeric matrix materials used in the composites industry, including epoxies, vinyl esters, unsaturated polyester resins (UPRs) and phenolic resins, play important roles in developing high performance composite materialsin various industries [1]. Unsaturated polyester resins, recognized for their cost-effectiveness and ease of processing, are generally categorized into orthophthalic, tereph-

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thalic, and isophthalic types, each having a distinct thermal and chemical properties [2]. In the area of construction and building materials, orthophthalic resins are known for their low thermal stability and chemical resistance, while isophthalic resins exhibit superior quality, showcasing better chemical, thermal resistance, and flame resistance [2]. Similarly, terephthalic resins, derived from terephthalic acid or its dimethyl ester, have high chemical inertness and resistance to harsh environmental conditions, making them ideal for applications requiring long-term durability and reliability [1,2]. Despite these advantages, the enhanced properties of isophthalic resins are generally considered lower than those of epoxies which are often overpriced compared to polyesters and vinyl esters, mainly due to their exceptional mechanical properties and durability [1]. To achieve comparable engineering properties to epoxies, blending as a cost-effective method within the composite industry is often advocated [3]. Moreover, blending not only addresses cost concerns but also offers a versatile approach to enhance the properties of resulting polymer composites, proving valuable for various applications [4,5].

Blending, recognized as a readily achievable and cost-effective method for developing high-performance polymer resins, stands out among various techniques, such as reinforcements and additives [4,5]. This method involves the creation of hybrid composites through the combination of two or more resins into a unified matrix, thereby enhancing properties and furnishing adaptability for an array of applications [6–9]. The efficacy of this process is dependent upon critical factors including the nature of hybrid polymers, their relative proportions, degree of miscibility, and the details of the blending procedure [4,5]. Polymer blends, classified into fully miscible, partially miscible, and entirely immiscible types, have found applications across diverse industries, encompassing nanocomposites, electronics, and the plastic industry [10,11]. Despite the substantial body of research on high-performance polymer composites, to date, only a limited number of studies have systematically evaluated the comparative properties of blended polymer composites.

To develop materials with enhanced properties compared to epoxies, there have been numerous attempts in the literature using various methodologies, such as blending, reinforcements, and the incorporation of antioxidants, plasticizers, or processing agents [3]. Among these approaches, the deployment of hybrid (blending) polymer resins has emerged as a simple and economically viable strategy for fabricating high-performance polymer resins, particularly when used with single-phase resins [4,5]. This methodology involves the synthesis of hybrid composites by combining two or more resins and reinforcing them into a consolidated matrix [6–8]. This systematic approach not only enhances the properties of resultant polymer composites but also facilitates adjustments in the workability of thermally sensitive polymers and the impact resistance of homopolymers, among other versatile applications [9].

A brief overview of the literature shows that the blended system of epoxy–vinyl ester resins combined with various unsaturated polyesters have not yet been conducted. To bridge this research gap, the current study intends to contribute to the literature by generating binary and ternary blends involving a diverse range of unsaturated polyester resins alongside bisphenol-A-based epoxy-vinyl ester resins. In the process of blending of polymers, several factors play a crucial role in determining the performance of the resulting composites [4,5]. These factors include the types of hybrid polymers employed, their relative proportions, degree of miscibility, inherent characteristics, amount of compatibilizer, and the intricacies of the blending procedure. Accordingly, polymer blend types may be categorized into three distinct classifications of: fully miscible blends, partially miscible blends, and entirely immiscible blends. Additionally, these polymer blends may exist in either a homogeneous or heterogeneous state. In homogeneous blends, the average properties of the blend components are evenly distributed, while in heterogeneous blends, the properties of all blend components contribute to the resulting composite [10].

The versatility of polymer blends extends their applicability to many industries, including nanocomposites, electronic devices, the plastic industry, and supercapacitors, with predominant uses in areas such as adhesion, colloidal stability, and the design of composites and biocompatible materials [11]. Despite the evident potential, the comparative impact of blended composites has not been extensively explored within the domain of high-performance polymer composites. For example, Turcsan and Meszaros [12] achieved notable success, obtaining 15.5 % and 10.8 % higher tensile strength in hybrid mixtures containing epoxy and vinyl ester, resulting from the higher energy absorption of the epoxy-vinyl ester composite, and achieving good adhesion at the phase boundary. Cherian et al. [13] interpreted physical, mechanical, and thermal properties through synthesizing hybrid polymer structures incorporating unsaturated polyester resins and phenolic novolac epoxy resin, resulting in a significant increase of tensile strength and hardness properties. Similarly, other studies, including those by Kim et al. [14], Prabu and Alagar [15], and Ruban et al. [16], have demonstrated advancements in various aspects of hybrid polymer composites, illustrating the multifaceted potential of blending techniques. Balaji et al. (2020) investigated the mechanical and thermal properties of bagasse fiber/coconut shell particle hybrid bio composites reinforced with cardanol resin and reported higher thermal stability, as a result of blending fiber-resin components [17]. Another study by Prabhu et al. (2021) examined the dynamic mechanical properties of Lannea Coromandelica blender hybrid epoxy composites, which were reinforced with silk, glass, pineapple, flax, and glass fibers and reported a significant improvement of composite stiffness and adsorption energy [18]. Additionally, Prabhu et al. (2022) conducted research on the mechanical, thermal, and morphological analysis of hybrid natural and glass fiber-reinforced hybrid resin nanocomposites and showcased the superior mechanical properties of blending technique [19]. Other researchers [20,21] have also underscored the benefits of blending polyamide, polyacrylates, chlorinated, and nitrile rubber with thermoset epoxy–unsaturated polyester resins, showcasing improvements in compatibility, corrosion resistance, and mechanical properties compared to unblended resins.

In this context, the present study makes a significant contribution by systematically evaluating the properties of a group of differently produced composites, thereby uncovering the potential of blended systems for hybrid polymer composites. This includes the use of blended systems including epoxy–vinyl ester resins mixed with various unsaturated polyesters to comprehensively assess the impact of polymer blends on hybrid polymer composites. In addressing this research gap, our study undertook the production of a variety of composites, specifically binary and ternary blends encompassing different polymer types. This includes variations of orthophthalic, isophthalic, and terephthalic unsaturated polyester resins in conjunction with bisphenol-A-based epoxy-vinyl ester resins. To evaluate the properties of these produced composites, an extensive series of tests has been methodically developed and executed, covering evaluations in physical, chemical, thermal, and mechanical domains. The following sections provide a detailed information about the testing matrices employed and expands upon the results obtained from these comprehensive assessments.

## 2. Material and methods

### 2.1. Materials

In this research, the selection of base resins was based on careful consideration of key properties essential for the study. For instance, the orthophthalic polyester resin (POLIPOL 3562-SR), isophthalic polyester resin (POLIPOL 3873-SR), and terephthalic polyester resin (POLIPOL 3570-SR) were chosen due to their specific gravity, solid content (43 %, 42 %, and 42 % respectively), and commercial availability from Poliya Polyester Industry and Trade Ltd. Sti. in İstanbul, Türkiye. Additionally, a bisphenol-A-based epoxy vinyl ester resin (POLIVES 701) was selected for its specific gravity (1.044 g/cm$^3$), 42 % solid content, and commercial availability from the same supplier. The choice of these resins was made to ensure a diverse range of properties in the resulting blends, considering factors such as cost-effectiveness and ease of processing.

### 2.2. Specimen preparation and testing methods

A total of fourteen composite sheets were produced, incorporating orthophthalic, isophthalic, terephthalic, and epoxy-based vinyl ester resins with a thickness of 4 mm. The resin mixtures were poured into molds (dimensions of 400 mm × 300 mm × 4 mm), and after curing, the composite sheets underwent testing for various physical, chemical, thermal, and mechanical properties. The experimental work plan and the image of the experimental preparation process are detailed in Table 1 and Fig. 1, respectively. Next, mixtures totalling 550g were homogeneously mixed for 3–5 min in a glass beaker. Cobalt Octoate Accelerator KP6, at a rate of 1 % by weight of the total resin, was added and stirred for 2–3 min, followed by the addition of the initiator, MEKP, at a rate of 1.5 % by weight of the total resin Figs. 2–4. The entire mixture was kept under laboratory conditions for 12 h for initial curing based on ISO 291 [22]. The hardened composite sheets underwent a further curing process in the oven for 3 h (1 h at 50 °C, 1 h at 80 °C, and finally 1 h at 110 °C), as noted in Fig. 5. Subsequently, specimens were cut to the dimensions specified in the relevant standards for physical, chemical, thermal, and mechanical properties testing.

## 3. Testing methods

A summary of the tests and the corresponding standards is presented in Table 2, and subsequent sections offer additional information about the equipment and testing procedures.

### 3.1. Physical tests

To evaluate material properties comprehensively, physical tests were conducted, including gelation time (ISO 2535), gelation temperature (ASTM D3056), peak exotherm temperature (ASTM D2471), and viscosity (ISO 2555) [23–26].

### 3.2. HDT analyses

Thermal tests, specifically HDT analyses, were performed following ISO 75-1 standards using a computer based HDT/Vicat standard device. The average HDT temperature was recorded after testing three samples [27].

### 3.3. Barcol hardness tests

The Barcol hardness tests were conducted using a GYZJ-934-1 type Barcol hardness device, following ASTM D 2583, a method designed for assessing the hardness of both reinforced and unreinforced rigid plastics [28]. At least three hybrid resin samples with dimensions [30 mm × 30 mm × 4 mm] were examined. The Barcol hardness tests for these samples involved placing the plates on a

**Table 1**
Presenting the mixture number, sample names, and sample components used in this study.

| Mixture No. | Sample names | Sample Component |
|---|---|---|
| 1 | O | Orthophthalic Polyester Resin |
| 2 | I | Isophthalic Polyester Resin |
| 3 | T | Terephthalic Polyester Resin |
| 4 | V | Vinyl ester Resin |
| 5 | OV | Orthophthalic + Vinyl ester Resin |
| 6 | IV | Isophthalic + Vinyl ester Resin |
| 7 | TV | Terephthalic + Vinyl ester Resin |
| 8 | OI | Orthophthalic + Isophthalic Resin |
| 9 | OT | Orthophthalic + Terephthalic Resin |
| 10 | TI | Terephthalic + Isophthalic Resin |
| 11 | OIT | Orthophthalic + Isophthalic + Terephthalic Resin |
| 12 | OIV | Orthophthalic + Isophthalic + Vinyl ester Resin |
| 13 | TIV | Terephthalic + Isophthalic + Vinyl ester Resin |
| 14 | OTV | Orthophthalic + Terephthalic + Vinyl ester Resin |

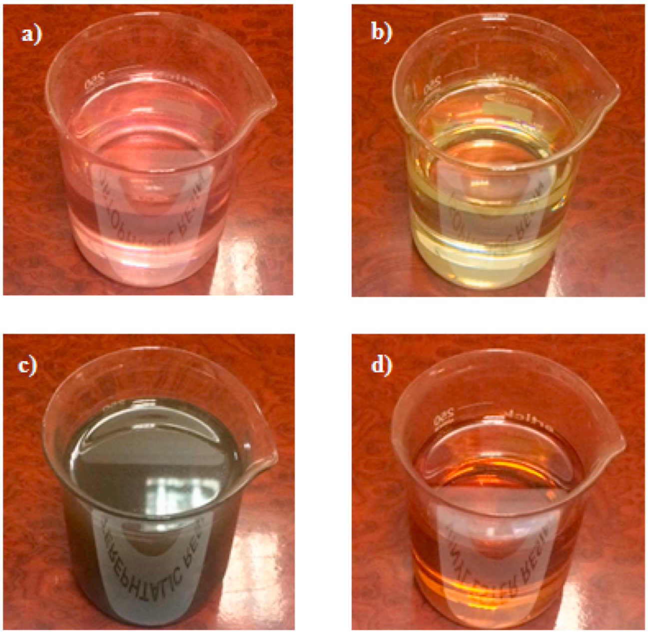


**Fig. 1.** a): Orthophthalic polyester, b): Isophthalic polyester, c): Terephthalic polyester, and d): Vinyl ester.

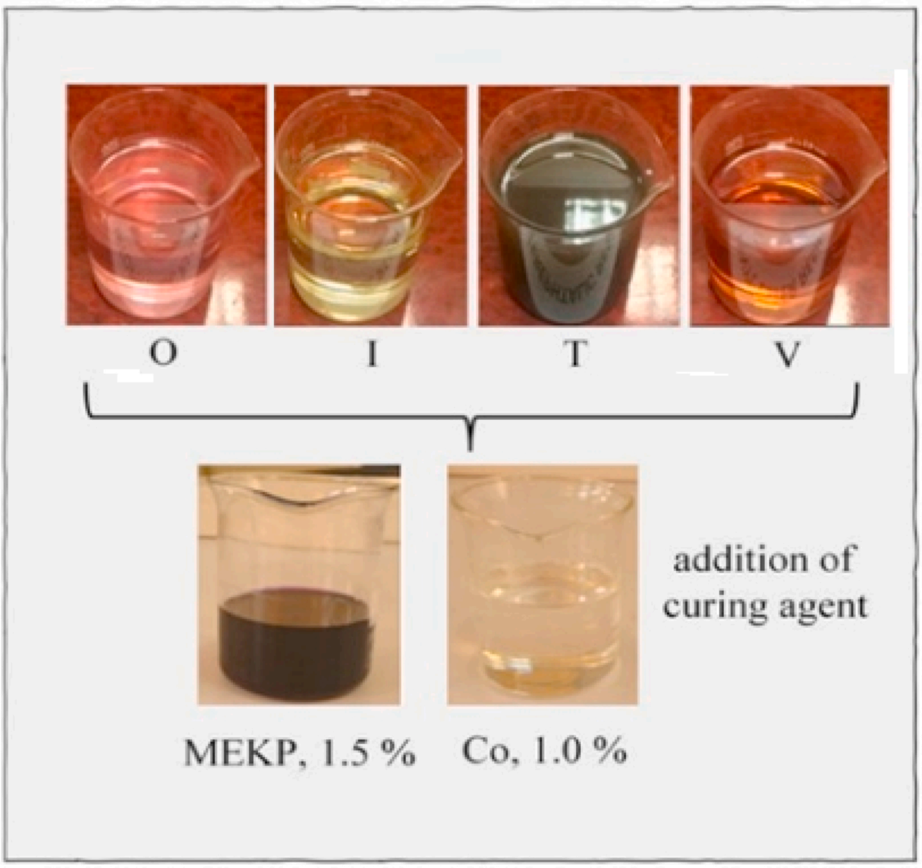


**Fig. 2.** Polymerization process.

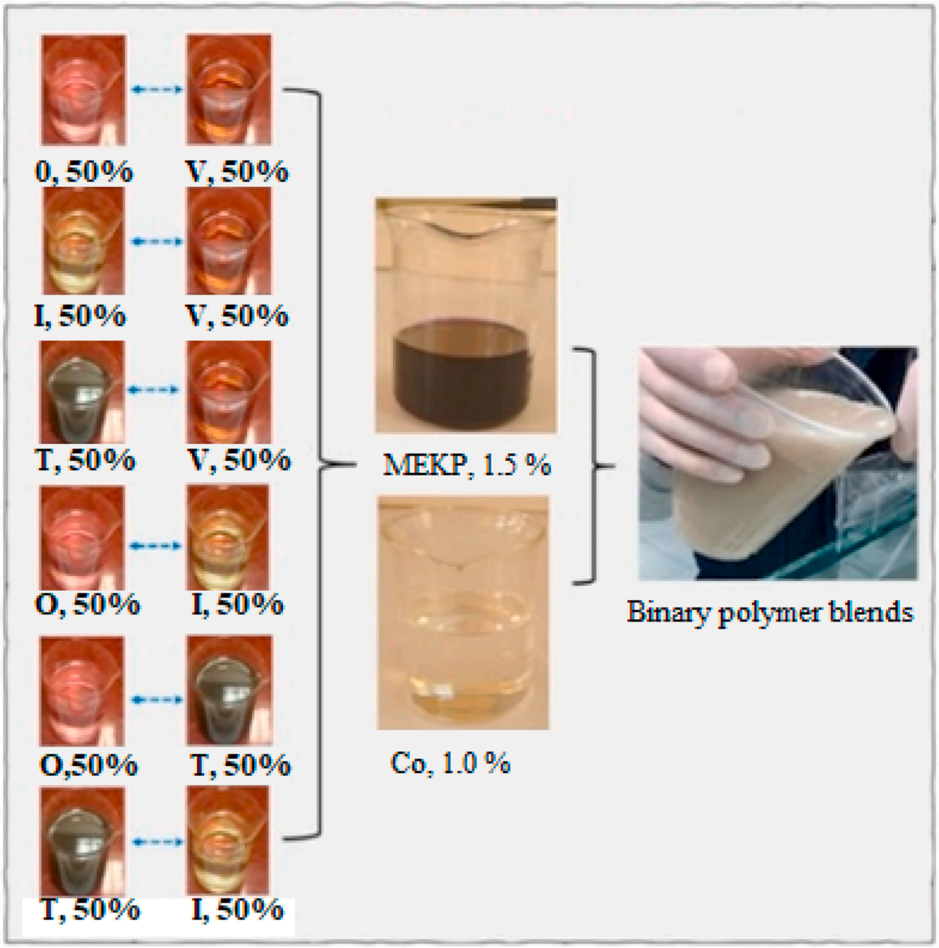


**Fig. 3.** Hybridization process of binary polymer blends.

level surface and conducting the examination with a Barcol Hardness apparatus (commercially known as GYZJ-934-1 type), adhering to the procedural guidelines outlined in the ASTM D 2583 standard method. The plates were precisely aligned perpendicular to the surface and securely affixed in place. The apparatus held firmly, registering an incremental increase in its dial indicator through the manual application of downward force over the casing until the dial reached its maximum position. Subsequently, the recorded peak reading was meticulously documented.

### 3.4. *Charpy impact strength tests*

To evaluate the impact resistance of samples, Charpy impact strength tests for unnotched specimens were carried out according to ISO 179-1 standards [29]. The Charpy impact test is generally used to determine the resistance capacity of a material against impact loading. It measures the required amount of energy to break a material, which can be used to compare the impact strengths of various materials. The test is conducted on a minimum of three specimens from the same batch (based on the standard), and the results are used to determine whether the material is brittle or ductile. Factors affecting Charpy impact energy include yield strength, notch shape and depth, and temperature [30].

### 3.5. *Tensile tests*

Tensile tests were conducted at a test velocity of 1 mm/min, adhering to ISO 527-1 standards [31]. The tensile test samples of plate-shaped non-fibrous hybrid resin mixture and fibrous hybrid resin mixture were carefully extracted from the mold and precisely cut using a diamond-tipped mechanical cutting device, conforming to analysis standards. After a 3-day waiting period at room conditions, the samples underwent tensile testing, with a minimum of 3 specimens cut for each mechanical test. The tensile test was performed at a test speed of 1 mm/min in accordance with ISO 527-1 standards Fig. 6.

The cutting process of the extracted samples from the mold was automated by entering the desired dimensions into a computer program and executed with a specialized cutting device, as depicted in Fig. 7.

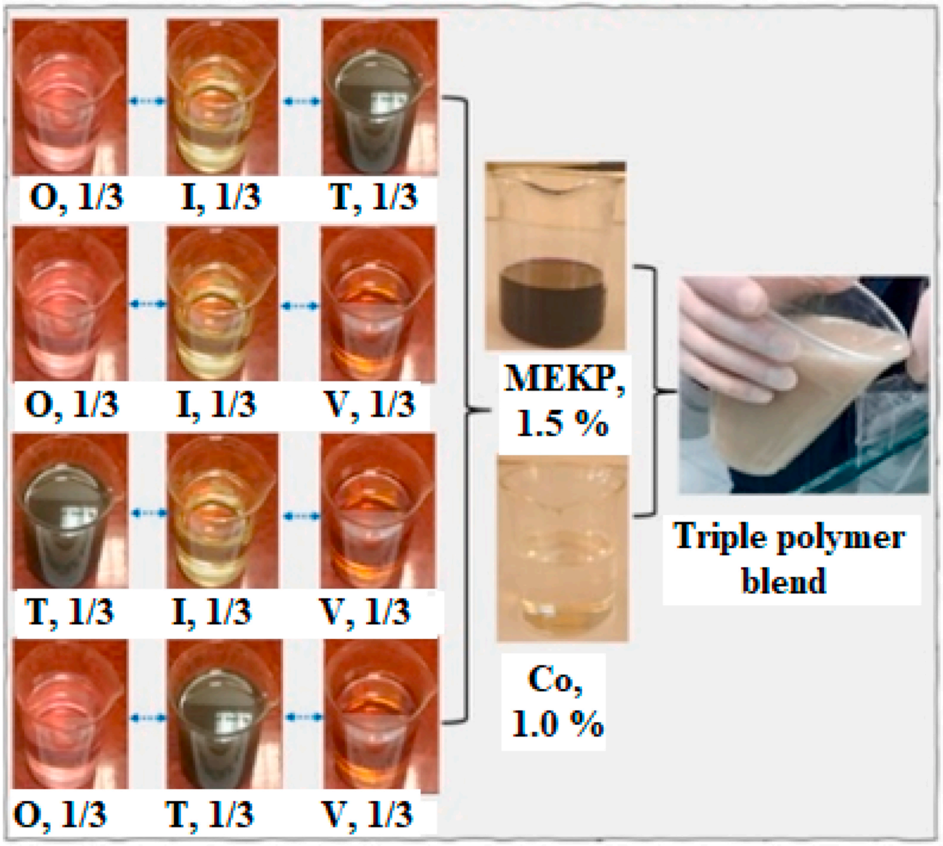


**Fig. 4.** Hybridization process of triple polymer blends.

Measurements of thickness, width, and length for all samples subjected to mechanical testing were conducted with a digital calliper, providing precision up to 0.01 mm. Visual representations of the mechanical test samples cut from resin mixtures were presented in Fig. 8.

### 3.6. Flexural tests

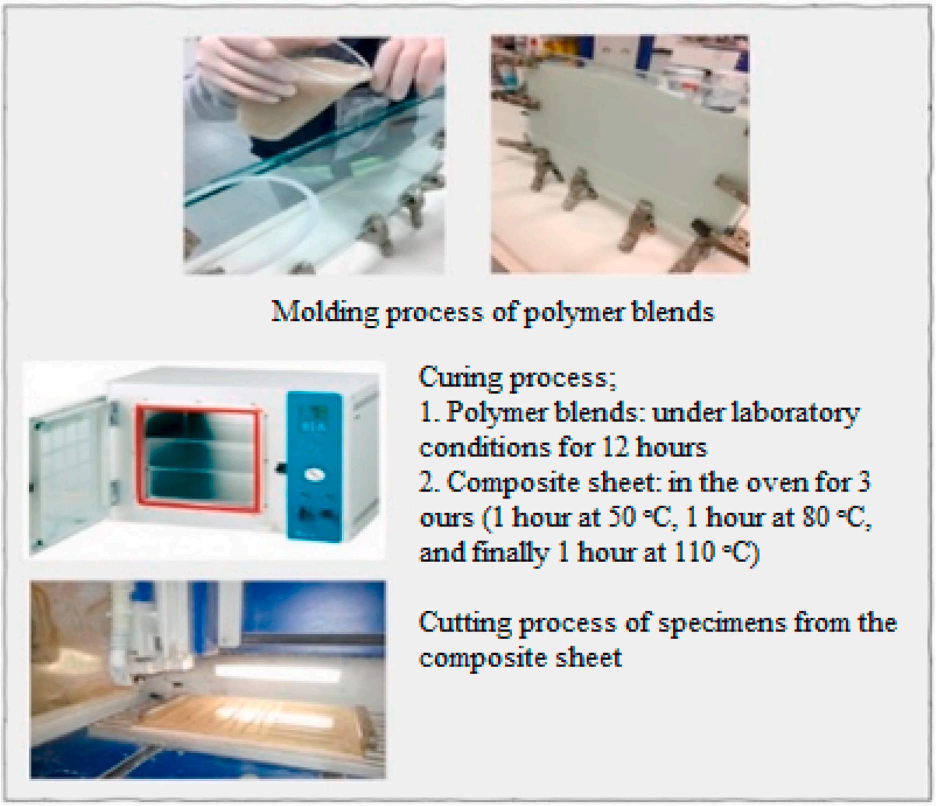
Flexural strength tests were conducted at a controlled test velocity of 2 mm/min, adhering to the ISO 178 standard [32]. Specimens designated for the flexural strength test, representing both plate-shaped non-fibrous and fibrous hybrid resin mixture, were carefully extracted from the mold and tailored to meet the specified standards. They were then cut using a precision diamond-tipped mechanical cutting device. Following a requisite of 3-day maturation period under ambient conditions, the prepared specimens underwent systematic testing. For each individual mechanical test, a minimum of three specimens were cut from the fully cured resin plates. The entire flexural testing procedure was executed in accordance with the ISO 178 [128] standard, with a test speed of 2 mm/min throughout the evaluation. The dimensions of the specimens used for the flexural strength test were meticulously crafted to meet the exacting specifications of 100 mm × 80 mm × 4 mm in millimetres.

### 3.7. FT-IR tests

The FT-IR test was conducted using a Shimadzu IR-Prestige 21 device with a resolution of 4 $cm^{-1}$ and 20 scans. This analysis aimed to investigate the characteristic structures and polymer behaviour of the samples. The electromagnetic spectrum in the range of 600–4000 $cm^{-1}$ was scanned by compressing the solid samples with a certain pressure against a Zn–Se crystal. The resulting FT-IR spectra were then analyzed to identify molecular absorption peaks, providing insights into the composition and molecular interactions within the composite materials.

### 3.8. SEM analysis

Scanning Electron Microscopy (SEM) analysis was conducted using the FEI Quanta FEG 250 model equipment at the Scientific and Technological Research Application and Research Center (DÜBİT).



Molding process of polymer blends

Curing process;
1. Polymer blends: under laboratory conditions for 12 hours
2. Composite sheet: in the oven for 3 ours (1 hour at 50 °C, 1 hour at 80 °C, and finally 1 hour at 110 °C)

Cutting process of specimens from the composite sheet

**Fig. 5.** Molding, curing, and cutting processes.

**Table 2**
Presents the tests conducted and the standards followed.

| Test | Standard Followed |
|---|---|
| Gelation time | ISO 2535 |
| Gelation temperature | ASTM D3056 |
| Peak exotherm temperature | ASTM D2471 |
| Viscosity | ISO 2555 |
| Heat deformation temperature (HDT) | ISO 75 |
| Barcol Hardness | ASTM D2583 |
| Charpy impact strength | ISO 179 |
| Tensile strength and modulus of elasticity | ISO 527 |
| Flexural strengths | ISO 178 |
| FT-IR | – |
| TGA – DTA | – |

### 3.9. *TGA/DTA analysis*

Thermogravimetric and differential thermal analyses (TGA/DTA) were performed utilizing a DTG 60H - DSC 60TGA model device manufactured by Shimadzu.

## 4. Results and discussion

### 4.1. *Gel time*

The results of the gel time analysis are depicted in Fig. 9. The figure illustrates mean gel times for single, binary, and ternary resin mixtures, recorded as 17.0, 15.7, and 16.8 min, respectively. It is observed that, on average, the gel time of single resin within mixtures exceeds that of both binary and ternary counterparts. This phenomenon may be attributed to the comparatively lower gel time exhibited by terephthalic resins relative to other resin types and formulations. Similarly, mixtures incorporating orthophthalic, isophthalic, and terephthalic variants exhibit mean gel times of 15.9, 15.2, and 15.1 min, respectively, in contrast to the 19.1 min observed for vinyl ester resin samples. This collective finding implies that, in general, all variants of polyester resin manifest significantly shorter gel times than epoxy-vinyl ester composites.

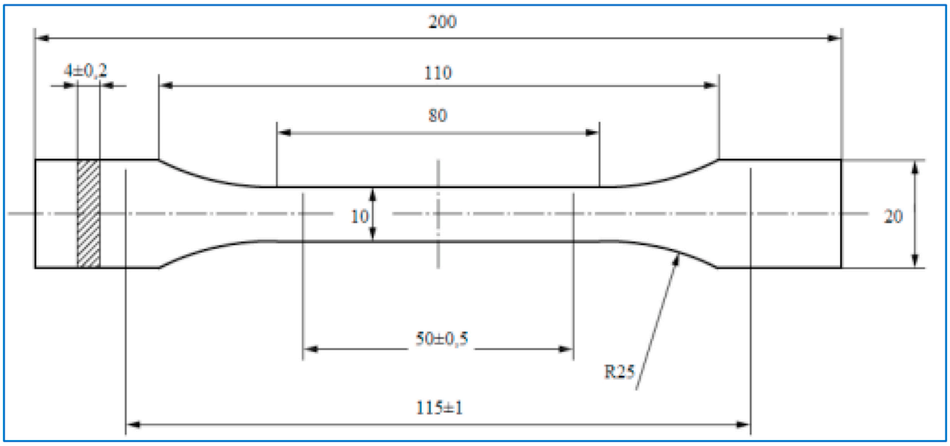


**Fig. 6.** Specimen dimensions subjected to tensile strength test.

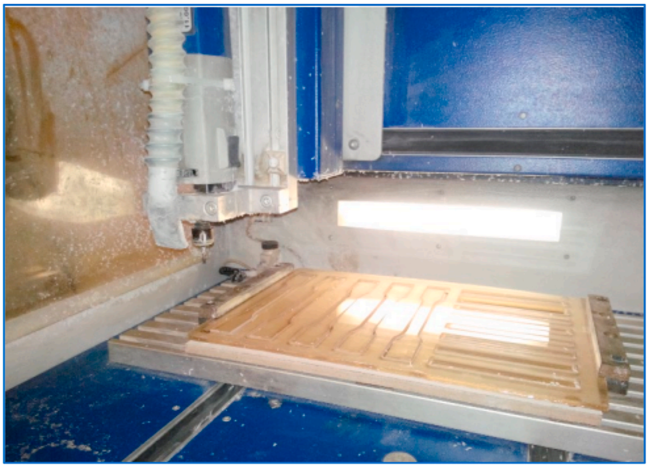


**Fig. 7.** Cutting device.

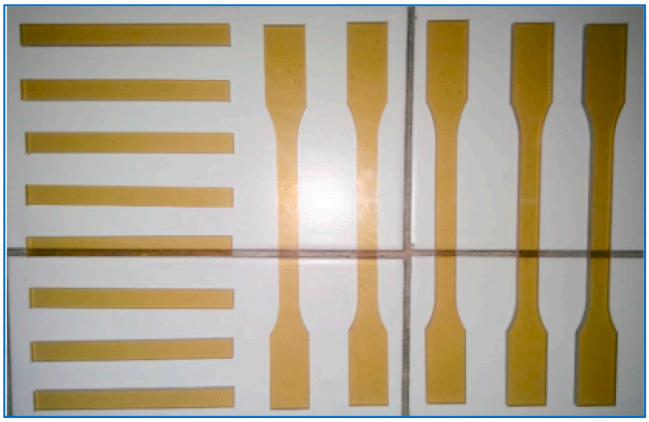


**Fig. 8.** Resin flexural and tensile strength test specimens.

Furthermore, consistent outcomes with regard to distinct initial gelation rates have been corroborated by previous studies, as referenced in Refs. [33,34], indicating a slow pace of cross-linking subsequent to the initial gelation. Nevertheless, it is noteworthy that, overall, the gelation time of vinyl ester resin tends to be relatively lengthier compared to alternative resin formulations. This protracted gelation duration may be attributed to inherent structural differences in vinyl ester resin or variations in the composition, including divergent quantities of additives such as inhibitors present in the resin content.

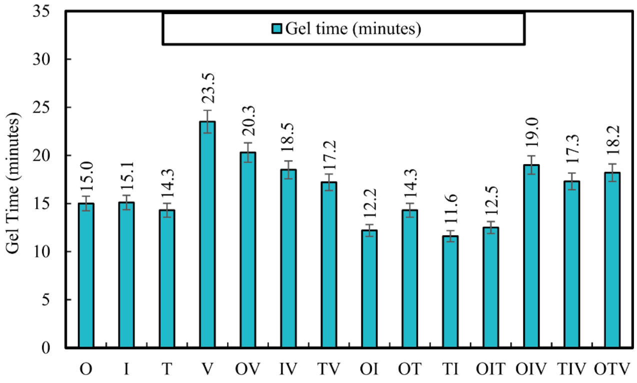


**Fig. 9.** Presenting the result of gel time based on ISO 2335.

### 4.2. Gel temperature

The outcomes of the gel temperature test, conducted in accordance with ASTM D3056 and presented in Fig. 10, reveal distinct temperature characteristics for single, binary, and ternary resin mixtures. The recorded gel temperatures are 30.1 °C, 31.3 °C, and 31.6 °C, for single, binary and ternary resin mixtures, respectively. This observation indicates that, on average, the reaction temperature of ternary resin mixtures surpasses that of single resin mixtures. This phenomenon is attributed to the establishment of cross-chaining bonds as multiple polymer chains undergo bonding processes, as also shown by Refs. [33,35].

Further examination of the figure demonstrates that mixtures containing orthophthalic, isophthalic, and terephthalic variants exhibit gel temperatures of 30.3 °C, 31.3 °C, and 31.3 °C, respectively. In contrast, epoxy-vinyl ester mixture composites exhibit a mean temperature of approximately 32 °C. This difference highlights that orthophthalic polyester resins exhibit lower gel temperatures, potentially contributing to superior shrinkage performance compared to extensively documented literature on vinyl ester resins [36,37].

### 4.3. Peak exothermic temperature

The outcomes of the Peak Exotherm Temperature analysis, as illustrated in Fig. 11, reveal notable temperature variations among reacting polymer resins. The highest and lowest temperatures experienced by these resins are recorded as 190 °C and 180 °C, respectively, with the former associated with terephthalic polyester and the latter observed in both orthophthalic and isophthalic polyesters combined with vinyl ester resins. Notably, the most substantial temperature difference is observed between orthophthalic and terephthalic resins, amounting to a significant 10 °C difference. This difference may be attributed to variations in the polymer chain bonding mechanisms between the two resin variants. Additionally, samples produced with vinyl ester resins exhibit the second-lowest temperature for bonding mechanisms compared to other resin types.

This observed trend is further evident in binary and ternary mixtures containing vinyl ester, exhibiting a mean peak exothermic temperature of 183 °C, as opposed to 183.2 °C, 185.0 °C, and 184.4 °C for mixtures containing orthophthalic, isophthalic, and terephthalic variants, respectively. It is well-established that resins generating higher exothermic heat are more susceptible to curing shrinkage and craze cracking [38].

### 4.4. Viscosity

Fig. 12 illustrates the viscosity values for various polymer blends produced in this study. The highest viscosity, approximately 400 cP, is noted in vinyl ester-based resins, while the lowest, at 234 cP, is attributed to terephthalic resin samples. It can be seen that, the mean viscosity values for single resin versus binary resin are closely comparable (295 cP versus 294.5 cP). However, a

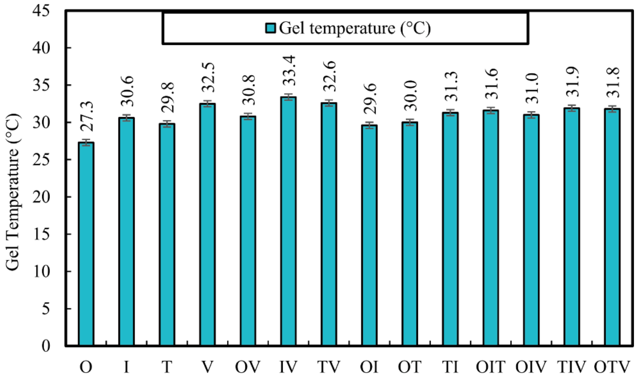


**Fig. 10.** Presenting the result of gel temperature test based on ASTM D3056.

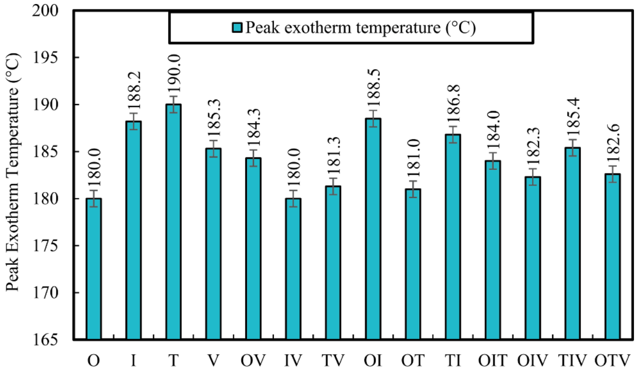


**Fig. 11.** Presenting the result of Peak exotherm temperature test based on ASTM D2471.

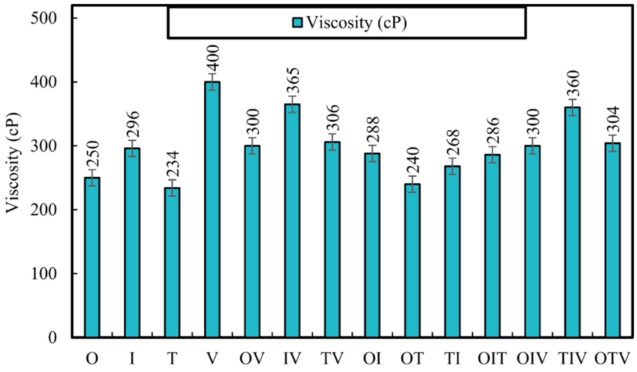


**Fig. 12.** Presenting the result of Viscosity test based on ISO 2555.

considerable shift is observed in ternary mixtures, with a viscosity of 312.5 cP being registered, indicative of the initiation of reactions and suggesting a dynamic viscosity response when three resins are combined. This perturbation aligns consistently, as blends containing vinyl ester consistently manifest the highest viscosity values, with a mean of 333.6 cP, reflecting the pronounced viscosity disparity of vinyl ester compared to other polyester variants. The term ‘potential initial reaction of polymer mixtures' is utilized to denote the observed viscosity shift during polymerization or blend formation, marking the inception of reactions. The heightened viscosity at 312.5 cP in ternary blends implies potential interactions and reactions among the three components, offering nuanced insights into the distinct characteristics of ternary resin mixtures. In conclusion, the results not only underscore the relevance of viscosity changes but also shows the intricate dynamics of polymer blends, particularly in ternary configurations.

### *4.5. Heat deformation temperature (HDT)*

HDT, which represents the upper limit of the dimensional stability of polymers without significant physical deformations under a normal load and thermal effect, provides important information for product design, including the working temperature of the resulting products [39]. It is affected by various factors, such as melting and mold temperatures, nucleating agents, and various process conditions, which are often associated with the mechanical behaviour of polymers [14]. The HDT values of the composite samples are given in Fig. 13. Based on the figure, it can be seen that in single-resin composites, the lowest HDT value (67.2 ˚C) was in the orthophthalic resin, and the highest one (91.3 ˚C) was in the isophthalic resin, representing a 24.1 ˚C difference. In binary hybrid composites, the lowest HDT value (78.9 ˚C) was in the orthophthalic – vinyl ester hybrid resin, and the highest one (94 ˚C) was in the isophthalic – vinyl ester hybrid resin resulting in 15.1 ˚C difference. When HDT test results made with ternary hybrid composites were ranked from lowest to highest; it was found 83.8 ˚C in the combination of orthophthalic, isophthalic and vinyl ester mixture, 84.1 ˚C in the orthophthalic, isophthalic, and terephthalic mixture, 84.5 ˚C in the orthophthalic, terephthalic and vinyl ester mixture, and finally 86.5 ˚C in the orthophthalic, isophthalic and vinyl ester mixture. This changes to a highest and lowest values of 86.5 ˚C and 83.8 ˚C, for ternary mixtures, respectively. Based on the mentioned, it is evident that the HDT values tend to be more aligned and merge toward a between value. Consequently, the hybrid mixture of resins commonly improved HDT values. This improvement indicates that intermolecular adherence and crosslinking are achieved at the desired level. These results appear to be consistent with the results of Refs. [14,16].

### *4.6. Charpy impact strength test*

The impact strength values of the composite samples are given in Fig. 14. As can be seen in the figure, the highest and lowest impact strengths values are found to be 11.18 kJ/$m^2$ and 6.29 kJ/$m^2$ in the epoxy-based vinyl ester resin and in the terephthalic resin

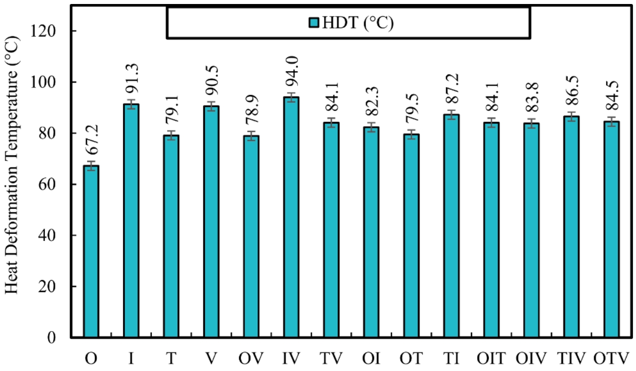


**Fig. 13.** Presenting the result of HDT test based on ISO 75.

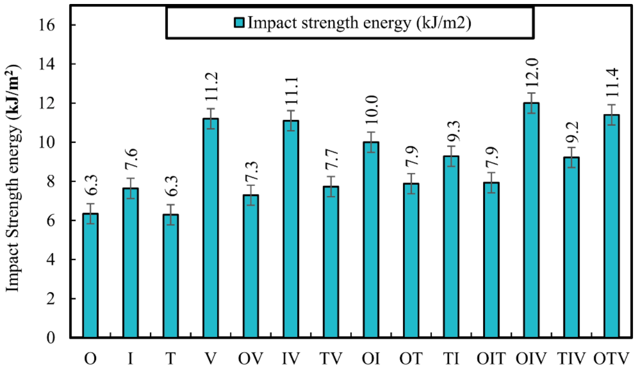


**Fig. 14.** Presenting the result of impact strength energy test based on ISO 179.

samples, respectively. This shows sharp differences between the polyester variances versus that of the epoxy-vinyl ester composite resin.

In binary hybrid composites, the lowest value (7.29 kJ/m$^2$) was found to be achieved for the orthophthalic – vinyl ester composite mixture, and the highest one, 11.12 kJ/m$^2$, was in the isophthalic polyester resin-based mixture. Similarly, in ternary hybrid composites, the lowest value achieved, 7.93 kJ/m$^2$, belonged to the orthophthalic, isophthalic, and terephthalic composite while the highest one, 11.98 kJ/m$^2$, was seen in orthophthalic, isophthalic composite. This shows that the mean value of single resin composite samples were smaller than binary and subsequently smaller than ternary mixes with the mean value for each is found to be 7.9, 8.9 and 10.1 kJ/m$^2$, respectively. These results appear to be consistent with the results of [15,21].

### 4.7. Tensile strength

The outcomes of tensile strength and modulus of elasticity tests conducted on composite samples, are shown in Figs. 15 and 16, respectively. Fig. 15 illustrates the tensile strength results, where the minimum value of 72 MPa is observed in the terephthalic resin mixture for single-resin composites, and the maximum value of 77 MPa is noted in the epoxy-based vinyl ester resin. In binary hybrid composites, a range of 72.4 MPa–77.2 MPa is observed, with the former belonging to the orthophthalic-terephthalic composite mixture, and the latter in the terephthalic-isophthalic composite mixture. Ternary hybrid composites exhibit a broader spectrum, with

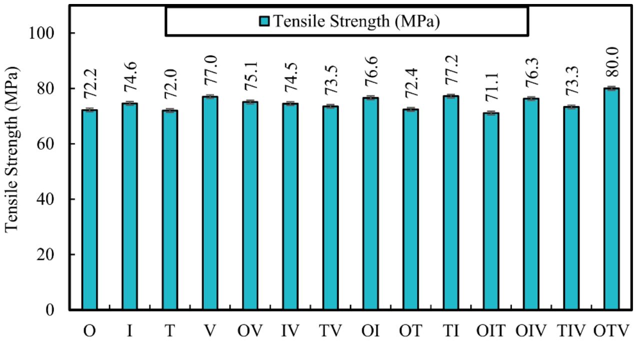


**Fig. 15.** Presenting the result of tensile test based on ISO 527.

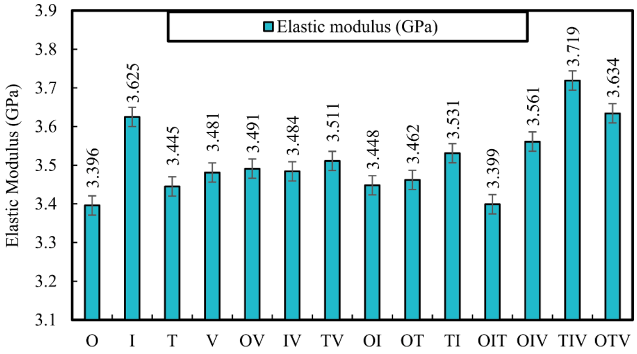


**Fig. 16.** Presenting the result of elastic modulus test.

the lowest and highest tensile strengths, 71.1 MPa and 80.0 MPa, respectively, attributed to orthophthalic-isophthalic-terephthalic and orthophthalic-terephthalic-vinyl ester composites.

The mentioned results indicate a substantial improvement in the tensile strength values of hybrid resin composites compared to single resin composites, similar to the findings documented in Refs. [12–16]. This improvement can be resulted from the heightened energy absorption in binary and ternary hybrid composites and is further influenced by an increase in the degree of cross-linking, resulting in interlocking network structures through the expansion of polymer chains.

Based on Fig. 16, the highest and lowest values of elastic modulus is found to be 3.719 GPa and 3.396 GPa for terephthalic-isophthalic-vinyl ester composites from ternary mixtures and orthophthalic polyester from single resins, respectively. This observation mirrors trends noted in other tests, confirming the positive impact of the composite form the modulus of elasticity results. The mean values for single, binary, and ternary resins further show this observation, measuring 3.487 GPa, 3.488 GPa, and 3.578 GPa, respectively. Collectively, these findings underscore the positive influence of composite resin formulations on both tensile strength and modulus of elasticity, proving the potential benefits of hybrid integration in material science applications.

### 4.8. Flexural strength

The average results of the flexural strength test for composite samples are shown in Fig. 17, revealing distinctive patterns among single, binary, and ternary configurations. The mean flexural strength values are recorded as 128.6 MPa, 135.9 MPa, and 144.8 MPa, respectively. These findings are consistent with those presented in preceding sections, showing that the composite utilization of resins contributes to enhancing the physical-mechanical properties. This enhancement is believed to stem from the more effective crosslinking of polymer chains within epoxy-vinyl ester–polyester composites.

Further from the figure,it can be seen that composites formulated with orthophthalic, isophthalic, and terephthalic variants of polyester exhibit mean flexural strengths of 140.7 MPa, 138.0 MPa, and 134.2 MPa, respectively. In contrast, samples produced with epoxy-vinyl ester composites manifest an overall mean flexural strength of 141.7 MPa, marginally surpassing the values observed for polyester-based samples. According to previous studies, the degree of hardening is largely linked to the phase-separated morphology [40,41], alongside factors such as the type and proportion of the two components, as well as the shape, connectivity, and size of the domains [1,42]. In the context of this study, this relationship is attributed to the types of resins employed and their intrinsic polymerization tendencies when employed in composite form, with other variables maintained constant.

### 4.9. Barcol hardness

The results of the Barcol hardness test for polymer composites are shown in Fig. 18. It can be seen that the samples produced with terephthalic and orthophthalic polyesters exhibit the highest and lowest hardness values, measuring 46 and 42 HBa, respectively.

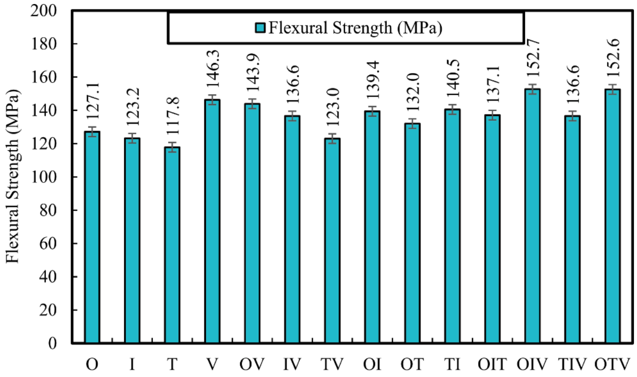


**Fig. 17.** Presenting the result of flexural strength test based on ISO 178.

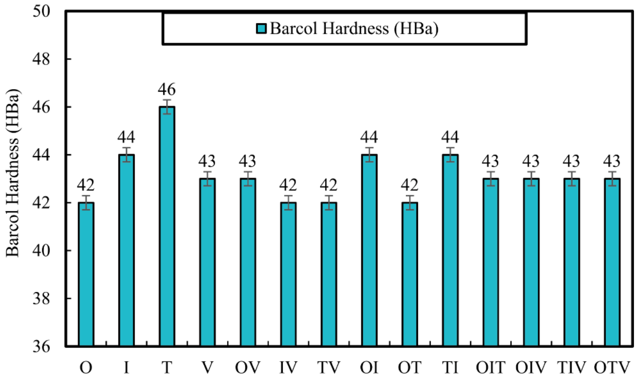


**Fig. 18.** Presenting the result of Barcol Hardness test based on ASTM D2583.

Consequently, the mean Barcol Hardness values for single, binary, and ternary mixtures are determined as 43.8, 42.8, and 43.0 HBa, respectively. Similarly, composite samples formulated with orthophthalic, isophthalic, and terephthalic variants of polyester resin manifest hardness values of 42.9, 43.3, and again 43.3 HBa, respectively. In contrast, composite mixtures produced with vinyl ester resin yield a mean hardness value of 42.7 HBa.

Although the adoption of binary and ternary resin combinations demonstrates a considerable enhancement in properties, it is seen that this improvement does not translate into pronounced variability in hardness values. This observation can be attributed to the high similarity in hardness values across various resin types, suggesting that it does not significantly alter the physical characteristics of the resulting composites. Similar findings have been documented in the literature [43,44].

### *4.10. FT-IR analysis*

Figs. 19–21 show the FTIR analysis results conducted on resin composites. Based on Fig. 19, it can be seen that distinct spectral features for single resin composites, such as orthophthalic, terephthalic, and vinyl ester are differentiable. The asymmetric stress vibration of υ(C = O) at 1716 cm$^{-1}$, υ(C–O) symmetrical tensile vibration at 1122 cm$^{-1}$, and υ(C = C) strain vibration at 1508 cm$^{-1}$ for vinyl ester are notable. Binary Hybrid Composites, shown in Fig. 20, including (OV), (TV), and (OT) resin mixtures, exhibited similar υ(C = O) and υ(C–O) vibrations. However, no apparent υ(C = C) peaks at 914 cm$^{-1}$ were observed. Flexural vibrations of $CH_2$ groups at 1456 cm$^{-1}$ were present in Fig. 20. Ternary Hybrid Composites such as (TIV) and (OTV) mixtures displayed an asymmetric stress vibration of υ(C = O) at 1725 cm$^{-1}$ and υ(C–O) tensile vibration at 1118-1120 cm$^{-1}$. Similar to binary composites, no clear υ(C = C) peaks at 914 cm$^{-1}$ were noted. The presence of flexural vibrations of $CH_2$ groups at 1456 cm$^{-1}$ is consistent in Fig. 21. Comparing the results, it can be stated that the cross-chained polymerization in binary and ternary mixtures, are supported by the absence of υ (C = C) peaks. Consistent υ(C = O) and υ(C–O) vibrations across mixtures indicates uniform molecular interactions, contributing to mechanical improvements. Intensity variations in $CH_2$ bands at 1456 cm$^{-1}$ further shows changes in polymer chain length, with longer chains correlating with enhanced mechanical properties which can be seen in binary and ternary composites.

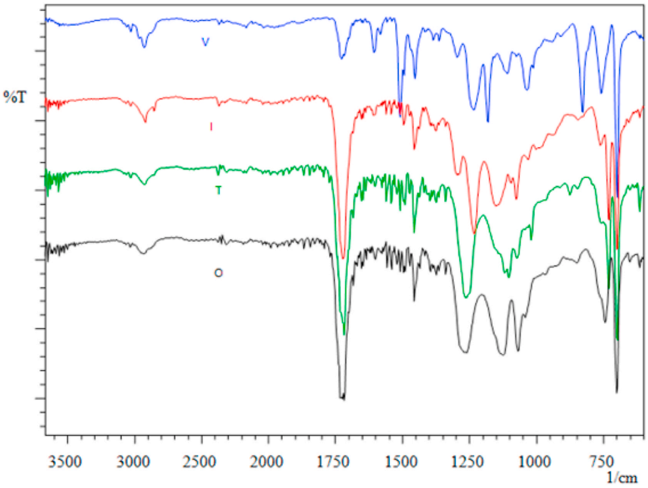


**Fig. 19.** FTIR spectrum of single resin composites.

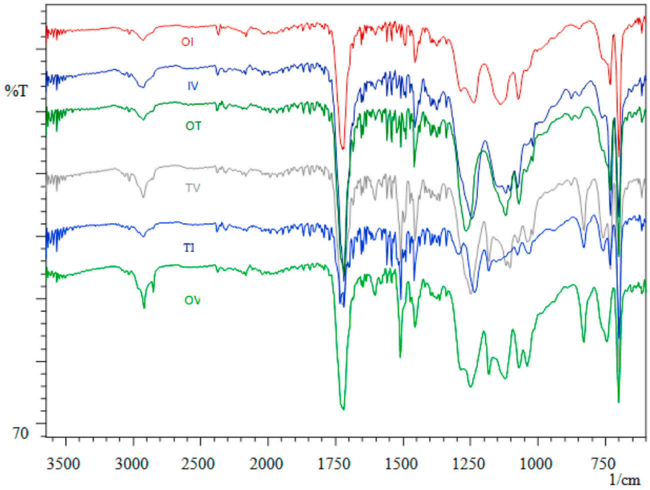


**Fig. 20.** FTIR spectrum of binary hybrid composites.

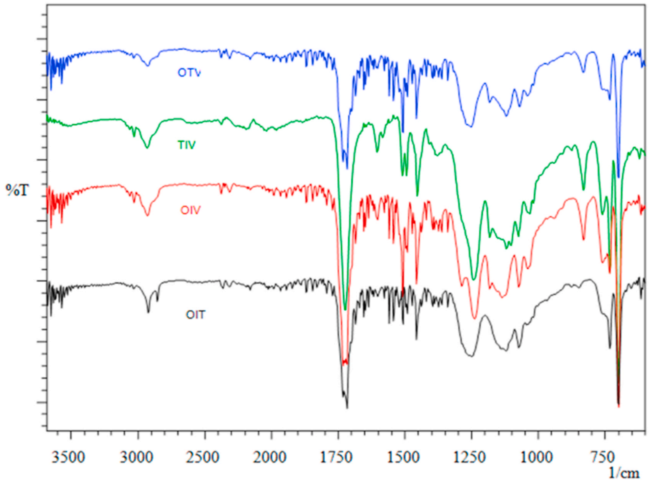
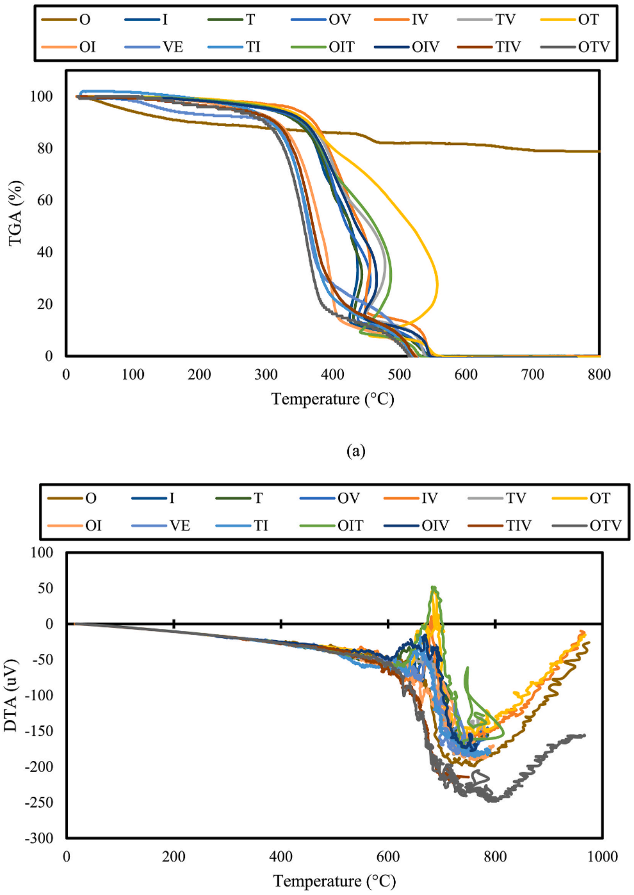


**Fig. 21.** FTIR spectrum of ternary hybrid composites.

### *4.11. TGA and DTA analysis*

Thermogravimetric analysis is a method of analyzing the thermal stability and decomposition behavior of materials. It functions based on the mass change of material over time when exposed to higher temperatures. In literature, TGA is most often used to evaluate thermal stability, provide a decomposition profile and kinetics, and even moisture content of the testing samples. Similar to TGA, Differential Thermal Analysis (DTA) provides information on endothermic (heat absorption) and exothermic (heat release) processes occurring in a given material. This can be done through studying the curvature derived from the temperature changes and associated heat flow in the system. In this regard, it is commonly established that an upward curvature represents heat absorption of samples from the surrounding area (endothermic – e.g., melting) and a downward deflection curve representing reactions that tend to release heat (e.g.,combustion).

Fig. 22 (a) presents the result of TGA on all mixtures. Based on the figure, the majoriy of resins expereince a two stage degradation, one at around 300 °C and the other at 400 °C. Similarly, almost all polymers experience a complete decomposition at around 500–600 °C. Nonetheless, it can be seen that the mixtures containing orthophthalic and isophthalic composites have performed better in the sense that they have been able to preserve higher mass at a given temperature than other combinations. In addition, the variation found is very subtle to provide conclusive evidence on such behavior, as the mixing duration, as well as other processes can have significant impact on the result of TGA on such hybrid composites. Fig. 22 (b) further presents the result of DTA tested on various mixtures. As can be seen in the figure, the highest endothermic behavior among the mixes is resulted from orthophthalic, isophthalic and terephthalic composite. In turn, the highest downward (exothermic) behavior is resulted from orthophthalic, terephthalic and vinyl ester composite and terephthalic, isophthalic and vinyl ester composite. From the figure, it can be seen that the inclusion of vinyl ester has on average resulted in higher downward DTA value while the combination of orthophthalic – terephthalic polyester has created more upward trend. This shows that samples produced with vinyl ester have released more heat than absorbed which can explain the reason for having been reported in literature as having a higher shrinkage ten-



(a)

(b)

**Fig. 22.** (a) TGA and (b) DTA result of various mixes.

dency than other resins [36]. The unexpected decrease in temperature observed in the TGA curves between 400 and 500 ˚C may be due to diverse factors influencing the thermal behavior of the polymer composites. Potential causes can be incomplete combustion or decomposition reactions of specific components within the resin mixtures, the presence of residual volatile components or impurities undergoing phase transitions, and not considered secondary reactions or side reactions not initially considered [45].

### 4.12. Scanning electron microscopy (SEM)

The adhesion morphology of the orthophthalic-vinyl ester, isophthalic-vinyl ester, and terephthalic-vinyl ester resins is given in Fig. 23, Fig. 24, and Fig. 25, respectively. As can be seen in the figure, at the 50 μm images, the orthophthalic polyester variance appear not to have a coherent and homogenous morphology. However, as the magnification is reduced (e.g., 100 and 200 μm) the mentioned features become less evident. Almost the same tendency can be seen for isophthalic-vinylester and terephthalic-vinylester SEM images. However, the isophthalic-vinylester and terephthalic-vinylester SEM images at 100 and 200 μm also present a considerably better surface morphology that can have been resulted from better adhesion and polymer crosslinking of isophthalic-vinylester and

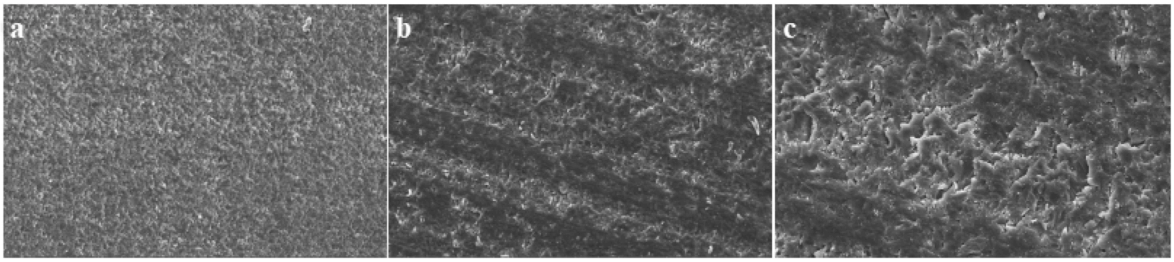


**Fig. 23.** Orthophthalic-vinylester SEM image; (a) 200 μm, (b) 100 μm, and (c) 50 μm.

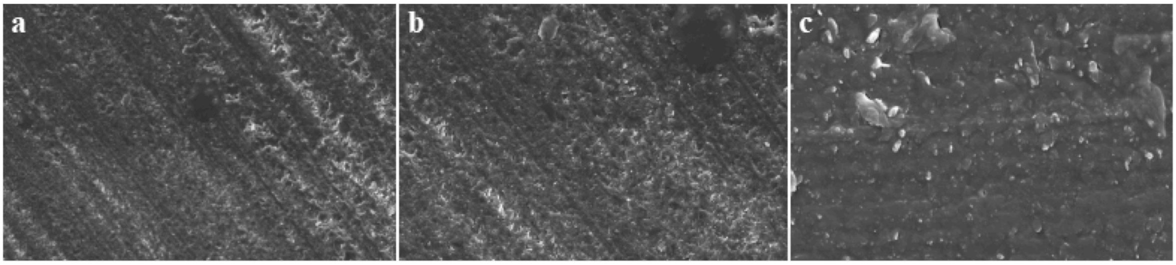


**Fig. 24.** Isophthalic-vinylester SEM image; (a) 200 μm, (b) 100 μm, and (c) 50 μm.

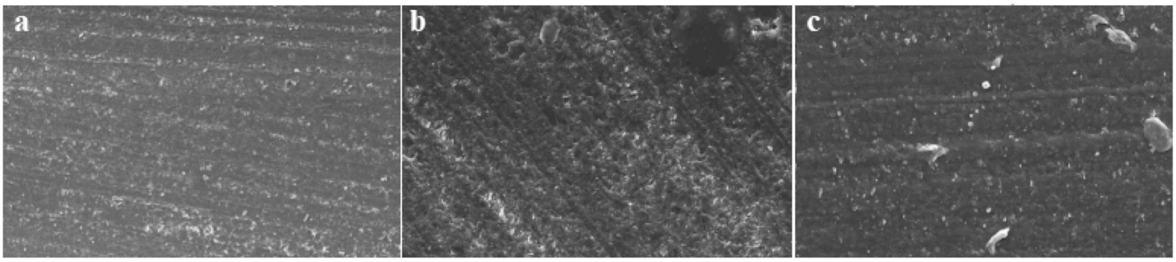


**Fig. 25.** Terephthalic-vinylester SEM image (a) 200 μm (b) 100 μm, and (c) 50 μm.

terephthalic-vinylester samples, as compared to those from orthophthalic-vinylester counterparts. Based on the above, it can be concluded that the terephthalic-vinylester composites have the most coherent and homogenous matrices with lowest content of air bubbles. Furture studies in this area can further attest to this using micro computerized tomography (CT scanning) to evaluate internal air bubbles featured and found in this study.

## 5. Conclusions

In this paper, a diverse group of hybrid polymer composites were synthesized by combining singular, binary, and ternary resins with distinct polymer types, including epoxy-vinyl ester and various polyesters (e.g., orthophthalic, isophthalic, and terephthalic variants). Samples were evaluated for their physical, chemical, thermal, and mechanical properties. Based on the results of this study, the following conclusions can be drawn.

- Marginally lower gel times in polyester resins compared to vinyl ester–epoxy composites were observed, and the hybrid utilization of resins in binary or ternary configurations yielded a modest reduction in gelation time while elevating overall gel temperature. Notably, lower gel temperatures were manifested in orthophthalic polyester resins, potentially contributing to enhanced shrinkage performance with regard to vinyl ester resins. Higher viscosity values were exhibited by vinyl ester–epoxy composites compared to polyester resins. A subtle nonlinearity was observed in the ternary deployment of resins, while binary samples demonstrated more linear interactions, influenced by the interplay of crosslinked polymeric chains and their temporal, thermal, and sequential interjections.
- Heat Deformation Temperature (HDT) and Charpy values were universally augmented by hybrid resin formulations, indicative of intensified intermolecular adherence and crosslinking. Subsequent marginal enhancements in tensile, flexural, and Barcol hardness tests were revealed to be dependent upon the phase-separated morphology and polymerization tendencies.
- Heightened polymerization was confirmed by Fourier-transform infrared (FT-IR) and scanning electron microscopy (SEM) analyses, signifying elongation of carbon chains in polymer structures with binary or ternary blends. Thermal analyses (TGA and DTA) unveiled endothermic and exothermic processes, with superior mass preservation at specified temperatures exhibited in orthophthalic and isophthalic composites. Conversely, greater heat release was observed in vinyl ester–epoxy composites, confirming the efficacy of binary or ternary polymer resin combinations in engineering high-performance polymer composites. Finally, substantial performance enhancement are achievable through binary and ternary resin blends, particularly those incorporating unsaturated polyester resins, that is underscored by this study, thereby providing valuable insights for optimizing the engineering properties of polymer composites.

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## Human and animal rights

Not applicable.

## CRediT authorship contribution statement

**Neslihan Gökçe:** Writing – original draft, Supervision, Project administration, Methodology, Resources, Investigation, Conceptualization. **Şevki Eren:** Writing – original draft, Project administration, Data Curation, Resources, Investigation. **Mehrab Nodehi:** Writing – original draft, Writing – review & editing, Visualization, Validation. **Doğu Ramazanoğlu:** Project administration, Data Curation, Resources, Investigation. **Serkan Subaşi:** Project administration, Data Curation, Resources, Investigation. **Osman Gencel:** Supervision, Project administration, Methodology, Writing – review & editing. **Togay Ozbakkaloglu:** Supervision, Project administration, Methodology, Writing – review & editing.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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