

Research Article

# Comparative Investigation of Epoxy-terminated and Carboxyl-terminated Butadiene Nitrile Rubber for Toughened Epoxy Resins

Purva Uniyal<sup>a</sup>, Piyush Gaur<sup>a</sup>, Jitendra Yadav<sup>a\*</sup>, Punya Bansal<sup>a</sup>, Neelanchali Asija Bhalla<sup>b</sup>

<sup>a</sup> Department of Mechanical & Aerospace Engineering, School of Advanced Engineering, Bidholi Campus, UPES, Dehradun, India – 248007

<sup>b</sup> Mechanical Engineering Department, School of Engineering and Applied Sciences, Bennett University, Greater Noida, UP, India – 201310

## ARTICLE INFO

### Article history:

Received:

Revised:

Accepted:

### Keywords:

CTBN;

ETBN;

Epoxy Polymer;

Toughness;

Recycled waste rubber

## ABSTRACT

The research presents how Carboxyl Terminated Butadiene Nitrile (CTBN) and Epoxy Terminated Butadiene Nitrile (ETBN) types of Reactive Liquid Rubber (RLR) influence epoxy resins through rheological, thermal, and mechanical property assessments. The use of recycled waste rubber creates sustainable high-performance additives through waste material transformation. Various mechanical, thermal, and rheological tests assessed the effects of CTBN and ETBN concentrations on their viscosity behaviour, mechanical properties, and curing process of the epoxy system used. The thermal stability of the ETBN and CTBN systems was analyzed by using Thermogravimetric Analysis (TGA) to determine decomposition temperatures and stability measurements. A complete set of mechanical tests measured tensile strength, flexural strength, and impact strength. Toughness improvements reached their peak with 2.5 wt.% ETBN addition resulting in a 42.2% increase in ultimate tensile strength, a 103.8% increase in tensile modulus, a 26.9% improvement in toughness, and a 67.65% increase in impact strength while maintaining all other properties. Also, 5 wt.% CTBN incorporation into the epoxy polymer leads to 30% increment in ultimate tensile strength, 49.5% increase in ultimate flexural strength, 68% increase in tensile modulus, and 300% increase in impact strength. So, both CTBN and ETBN are said to be effective tougheners that can be used to enhance the toughness of the overall matrix system while balancing other mechanical properties. The investigation highlights how the termination chemistry affects phase separation and interfacial adhesion, ultimately leading to improved performance for its applications in automotive and aerospace industries. The innovative use of recycled ETBN and CTBN thus creates a way for the development of sustainable solutions that deliver economic benefits and environmental advantages.

© 2025 The Author(s). Mechanics of Advanced Composite Structures published by Semnan University Press.

This is an open access article under the CC-BY 4.0 license. (<https://creativecommons.org/licenses/by/4.0/>)

## 1. Introduction

Epoxy-based composites have gained significant attention in various industries, including aerospace, automotive, marine, and construction, due to their excellent mechanical properties like strength and toughness, chemical resistance, corrosion resistance, and versatility in processing methods [1][2]. These composites consist of an epoxy resin matrix reinforced with short, long, or chopped fibres, which provide structural integrity and enhance the material's overall performance [3][4]. However, despite their many advantages in mechanical and thermal properties, epoxy resins inherently possess brittleness, which limits their application in environments where toughness and impact resistance are crucial [5]. Due to their brittle nature, these composites tend to crack easily. To overcome these limitations, toughening agents

like elastomers, thermoplastics, core-shell rubber particles, nanotubes, and nanoparticles are incorporated into the epoxy matrix system. These toughening agents have proved their worth in improving the mechanical properties, like fracture toughness and impact strength of composites, while significantly balancing the other properties, including their mechanical strength, like ultimate tensile strength, flexural strength, etc., and thermal stability. The selection and concentration (in volume or in weight) of toughening agents play a crucial role in calculating the final properties of the toughened epoxy composites. When RLR (Reactive Liquid Rubber) based tougheners like CTBN (Carboxyl-terminated-butadiene-nitrile) and ETBN (Epoxy-terminated-butadiene-nitrile) are incorporated into the epoxy resin, with a typical aim to enhance the overall toughness and impact strength of the cured matrix system [6]. This enhancement

occurs because of the rubbery nature of toughener-epoxy blended suspension, which is capable to absorb and dissipating energy, reducing the likelihood of brittle fracture[7][8]. Also, the rubbery phase gets deformed under the mechanical stress, further allowing the material to withstand high levels of strain without cracking and failing[9]. Hybrid toughening of epoxy glass fibre reinforced composites with CTBN and nano-silica was investigated[10]. Toughening mechanisms encountered were cavitation along with rubber particles and debonding of nanosilica, eventually leading to plastic void growth, which is considered a severe defect in composite material. CTBN successfully increases quasi-static interlaminar fracture energy, and reinforcement of nanosilica increases fatigue threshold strain energy release rate [11]. The ETBN toughened epoxy resin matrix system shows remarkably improved impact properties, that are energy absorbed before failure, toughness, and impact strength. This is because of the fact that, during the curing or solidification of the epoxy resin matrix system, phase separation occurs, and ETBN rubber particles tend to settle at the interface, because of which there is faster dissipation of energy as compared to other tougheners used [12]. Reactive liquid rubbers like ATBN [13], CTBN, ETBN, HTBN, etc., are low molecular weight elastomeric polymer materials that contain reactive functional groups like amine, epoxy, carboxyl, hydroxyl, etc. [14] [15]. These functional groups are capable of reacting and forming chemical bonds with other materials, like epoxy resin. These RLRs possess rubbery properties, which are beneficial for enhancing the toughness of epoxy resins. Rubbery properties refer to good elasticity, flexibility, allowing them to be soft and pliable, quicker in absorbing and dissipating energy [16]. The Bisphenol-A group of epoxy resin and the functional group of RLR have a synergetic behaviour on the toughness of epoxy resins [17] [18]. The innovation of utilizing CTBN and ETBN derived from recycled waste rubber offers significant environmental, economic, and industrial advantages, refer **Figure 1** [19]. By recycling waste rubber like tyres, industrial waste, or commercial waste, this approach of creating ETBN and CTBN and using it as filler material, supports sustainability and reduces landfill waste where burning of waste material is done, subsequently contributing to environmental conservation. Economically, this approach of reusing and repurposing ensures cost efficiency and opens up new revenue streams from discarded materials. In terms of performance, dual benefits can be achieved, one by enhancing the toughness and also balancing the structural integrity. An advanced material

recycling technique results in optimizing the production and application of CTBN and ETBN. Globally, this sustainable practice invigorates scalability and can be aligned with legislation and policies that promote circular economic principles. Overall, using CTBN and ETBN recycled rubber as a primary resource in the toughening of epoxy resin matrix system symbolizes a hands-on and impactful solution specially for the industries that have a demand to balance performance with sustainability. **Table 1** presents various toughening methods of epoxy resins based on literature, highlighting their significance, limitation and common toughening agents.

According to the literature, rubber modification has improved impact properties, but the thermal stability is reduced. Modification with thermoplastic materials as filler enhances the fatigue resistance, but the viscosity of the overall matrix system is reduced. Fillers like liquid crystal polymers helped in improving the crack resistance, but are very costly and found difficult to reinforce, may be due to weak adhesive properties. Other fillers like interpenetrating polymers provide a good balance of strength and toughness, but these are challenging to cross; maybe they are very difficult to disperse into the matrix systems. Core shell polymer material, like poly methyl methacrylate (PMMA) as a core material and poly methacrylic acid as a shell material, reduces internal stress but is affected by the particle size. Heat resistance is improved by adding thermosetting materials as tougheners, but they are very difficult to process. When block copolymers like styrene-butadiene-styrene are added, impact strength enhances because of the self-assembly mechanism. Nanoparticles, including zero-dimensional, one-dimensional, and two-dimensional particles like nanosilica, nanotubes, alumina, etc., are used as modifiers, which result in improved mechanical properties, but these face dispersion problems. Lastly, Organosilicon, when used as a modifier, helps in enhancing flame resistance and flexibility, but faces a blending problem.

The main objective of conducting this investigation is to enhance the toughness of low viscosity epoxy resin by incorporating Reactive liquid rubber-based tougheners into it. This study aims to investigate the flow behaviour and viscosity of the carboxyl-terminated butadiene nitrile and epoxy-terminated butadiene nitrile rubber toughened epoxy resin to understand their processing and application potential. Also, thermal properties are analyzed, including thermal stability, glass transition temperature (T<sub>g</sub>), and heat resistance to assess their suitability for high-temperature applications. The

evaluation of mechanical characteristics with a focus to determine influence of CTBN and ETBN on the structural performance of epoxy resin is also considered. The motivation for conducting this research stems from the need to develop epoxy-based composites with enhanced mechanical and thermal properties to meet the demand of high-performance applications. While substantial progress has been made in the toughening of epoxy resins, there remains a critical need for a comprehensive understanding of the relationship between the composition, structure, and properties of such materials. This understanding will enable the design and fabrication of a composite with tailored properties for specific applications. It has been reported several times that the incorporation of nanoparticles into epoxy resins leads to enhanced mechanical properties [20] [21]. So, in this study, an effort has been made to incorporate two different reactive liquid rubber CTBN and ETBN into epoxy resin. This study will help the researchers working on same field to understand the effect of these tougheners on the mechanical and thermal properties of epoxy resin. Both the tougheners are compared on the basis of their ultimate tensile strength, ultimate flexural strength, impact energy, and thermal properties. The best suitable toughener, along with its optimal concentration, is concluded in this study. Till now, very little literature is available on such types of thermoplastic toughening methods.

To conduct this investigation, 5 different formulations of CTBN and ETBN are chosen to be incorporated into CY 230-1 epoxy resin. 1%, 2.5%, 5%, 10%, and 15% by weight of these reactive liquid rubber-based tougheners are added and compared with the neat epoxy samples. The detailed description of samples, along with the nomenclature, has been provided in Table 6. The comparisons are studied on the basis of rheological, thermal, and mechanical properties. Rheological characterization includes

the study of properties like viscosity (in Pa-sec) and critical shear stress (in Pa), while thermal characterization includes the study of properties like onset decomposition temperature ( $T_{10\%}$  °C,  $T_{50\%}$  °C), maximum decomposition temperature ( $T_{max}$  °C), and weight loss %. Mechanical characterization gives the influence of CTBN and ETBN on properties like ultimate tensile strength (MPa), tensile modulus (GPa), ultimate flexural strength (MPa), impact strength ( $\text{kJ}/\text{m}^2$ ), and toughness ( $\text{MJ}/\text{m}^3$ ). The outcome of this study will be the evaluation of the best compatible toughener between CTBN and ETBN that will give the best balance of all the properties. Also, this study will evaluate the optimum formulation of the compatible toughener at which the best values of properties of toughened epoxy samples are obtained.

The novelty of this work includes the use of recycled waste rubber CTBN and ETBN into CY 230-1 epoxy resin, which will lower the production costs and will make epoxy resin more affordable for industrial applications. This study demonstrates an innovative approach to utilizing waste rubber in the form of value-added materials. No literature is available on the comparison and optimization of rheological, thermal, and mechanical properties of this low viscosity CY 230-1 epoxy resin incorporated with CTBN and ETBN.



Figure 1. CTBN and ETBN: Sustainable Derivatives of Recycled Rubber - INNOVATION, [22] [23] [24]

**Table 1.** Toughening methods along with their significance and limitations [25]

Toughening method	Significance	Limitations	Examples of toughening agents	Ref.
Rubber modification method	To improve the brittleness and cracking of cured epoxy To improve impact toughness and elongation	Reduces glass transition temperature, Young's modulus, and heat resistance	CTBN, ETBN, ATBN	[26] [27]
Thermoplastic modification method	To improve fatigue resistance, impact toughness, transverse tensile strength, and interlaminar shear strength,	Not easy to dissolve Increases viscosity, reduces thermal stability	Polystyrene, polyvinyl chloride, polypropylene	[28] [29][30]
Liquid crystal polymer modification method	Relaxes stress concentration at the crack end, hinders crack propagation This improves impact toughness	Costly Difficult in handling Difficult to achieve a reinforcing effect	Fibrils like Kevlar	[31][32]
Interpenetrating polymer network modification method	Molecular mixing occurs Have properties of different polymer systems Improves impact resistance, without sacrificing strength	The phase component is too large Challenging to achieve cross-linking	Copolymers or homopolymers systems are crosslinked to form a single polymer network.	[33][34]
Core-shell polymer modification method	Reduces internal stress, Improves bonding and impact strength	Greatly affected by particle size, concentration, and addition ratio.	Different combinations of core and shell Different properties can be achieved	[35][36][37]
Thermosetting modification method	Improves heat resistance and dimensional stability	High viscosity and difficult to process	Phenolic resin, polyamides, silicone	
Block copolymer modification method	Stable glass transition temperature Improves impact strength	Capable of forming self-assemblies and then nano-structures which affect mechanical properties	Acrylonitrile butadiene styrene, nitrile rubber	[38] [39] [40]
Zero-dimensional nano rigid particle modification method	Improves strength and other mechanical properties Gives reinforcement effect	Easy agglomeration, poor dispersion	SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub> , ZrO <sub>2</sub>	[41]
One-dimensional nano rigid particle modification method	High surface area of these 1D particles, so ease in stress transfer between matrix and fillers.	Easy agglomeration, disordered arrangement, and curling	Carbon nanotubes	[42]
Two-dimensional nano rigid particle modification method	Improves elastic modulus and failure strength Improves rigidity	Tends to agglomerate, difficult to disperse in epoxy resin	Graphene	[43] [44]
Organosilicon modification method	Flame retardant, heat resistant, high strength, flexibility, and chemically stable. Possess both organic and inorganic properties because of two different bonds.	Difficult to blend into each other	Organosilicon	[45]

**Table 2.** Materials selected for preparing toughened epoxy.

Sr. No.	Material and Chemical Formula	Commercial Name	Manufacturer/ Supplier
1.	Polymer material - DGEBA-based	Araldite CY-230/1 epoxy resin	M/S Excellence resins, Meerut. (U.P.) India
2.	Curing agent/ hardener - Amine-based	HY 951	M/S Excellence resins, Meerut. (U.P.) India
3.	Toughener I - Carboxyl Terminated Butadiene Acrylonitrile Reactive Liquid Rubber	EPOXY FINECURE CTBN	M/S Fine Finish Organics Pvt. Ltd., Mumbai, (M.H.) India

4.	Toughener II - Epoxy Terminated Butadiene Acrylonitrile Reactive Liquid Rubber	EPOXY FINECURE ETBN	M/S Fine Finish Organics Pvt. Ltd., Mumbai, (M.H.) India
----	--	---------------------	--

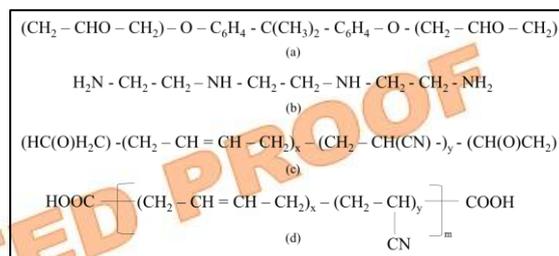
## 2. Materials and Methods

### 2.1 Material Selected

The base materials used in this study are CY230-1 epoxy resin, HY951 hardener, and reactive liquid rubber-based tougheners, as given in the Table 2 below. The materials used in the present study are DGEBA-based epoxy resin and AMINE-based hardener, serving as a primary polymer matrix system, both procured from M/S Excellence Resins, Meerut. To improve the toughness of epoxy resin, two rubber-based modifiers as tougheners are incorporated, i.e., CTBN and ETBN, both procured from M/S Fine Finish Organics Pvt. Ltd., Mumbai, (M.H.) India. These tougheners were chosen to enhance the thermal stability and mechanical properties of the overall polymer matrix system.

#### 2.1.1 Epoxy resin

DGEBA-based epoxy resin CY 230-1 is a high-performance material commonly used in a range of applications that demand excellent mechanical, thermal, and electrical properties. Its unique cycloaliphatic structure provides significant advantages over conventional epoxy resin, including lower viscosity, enhanced thermal stability, and better UV resistance. The absence of aromatic structures reduces susceptibility to UV degradation. Because of low viscosity, its processing is easier, and there is better impregnation into the fibres of the composite. This resin is capable of accommodating fillers like nanoparticles, etc., which are needed to carry out the current study. The fatigue resistance of CY 230-1 epoxy resin is very good, which is a very crucial property for materials where the application demands fluctuating and repetitive loads over time. This resin possesses high thermal resistance, making it capable of sustaining temperature variations. The epoxy resin used for the current study is Araldite CY 230-1, procured from M/S Excellence Resins, Meerut. (U.P.) India. The physical properties of this polymer system are given in Table 3. The chemical structure of this Di-Glycidyl Ether of Bisphenol A (DGEBA) type epoxy resin is shown in the Figure 2(a).



**Figure 2.** Chemical structure of (a) Di-Glycidyl Ether of Bisphenol-A based epoxy resin, (b) HY 951 Triethylene Tetramine, (c) Epoxy Terminated Butadiene Acrylonitrile, (d) Carboxyl Terminated Butadiene Acrylonitrile.

**Table 3.** Physical and chemical properties of epoxy resin CY230-1. [46] , Manufacturer provided

SN	Property	Value
1.	Viscosity at 25 °C	1350 mPa*s
2.	Density at 25 °C	1.1-1.2 g/cm <sup>3</sup>
3.	Appearance	clear liquid
4.	Epoxy content	4.20-4.35 eq./ kg
5.	Flash point	160°C

#### 2.1.2 Hardener

Amine-based hardener HY 951, which is commonly called triethylene tetramine, is used to facilitate curing and enhance the mechanical properties of epoxy resin. It has a molecular formula C<sub>6</sub>H<sub>18</sub>N<sub>4</sub>, molecular weight 146.23. It is also procured from M/S Excellence Resins, Meerut. (U.P.) India. It's a low viscosity liquid that provides strong adhesion, high chemical resistance, and excellent mechanical strength when mixed with epoxy systems. Typically, it is used in a ratio of 10:1 with epoxy resin by weight. HY 951 is widely applied in industrial, automotive, aerospace, and marine applications due to its ability to create durable and impact-resistant bonds. It also exhibits good thermal stability, making it suitable for high-performance composite structures and coatings. Figure 2(b) shows the chemical structure of HY 951 hardener. The physical properties of this hardener are given in the

Table 4.

**UNCORRECTED PROOF**

**UNCORRECTED PROOF**

**UNCORRECTED PROOF**

**Table 4.** Physical and chemical properties of amine-based hardener HY 951. [46], Manufacturer provided

SN	Property	Value
1.	Viscosity at 25 °C	10 mPa*s
2.	Density at 25 °C	0.98 g/cm <sup>3</sup>
3.	Appearance	clear liquid
4.	Flash point	110oC

### 2.1.3 Tougheners

Reactive Liquid Rubber (RLR) based tougheners like CTBN and ETBN are used as modifiers in the polymer matrix system with the motive to enhance the properties like toughness and impact resistance. CTBN contains a functional group of Carboxyl (-COOH), which helps in improving adhesion and flexibility, while the functional group Epoxy is contained by the ETBN, which possesses better compatibility with epoxy resin as it also contains the epoxy functional group. These tougheners enhance the flexibility, fracture toughness, and elongation properties of

These help mitigate brittleness in epoxy resins while maintaining their mechanical strength and chemical resistance. Proper formulation of these tougheners is essential to achieve the desired balance between toughness and stiffness in the final material. The chemical structure of ETBN and CTBN is shown in the **Figure 2(c)** and **(d)** respectively. The properties of these Reactive Liquid Rubber-based tougheners are stated in **Table 5**. The pictures of epoxy, hardener/ curing agent, CTBN, and ETBN are provided in **Figure 3**.

### 2.2 Fabrication of Toughened Epoxy Resin Samples

Six different formulations of CTBN and ETBN are mixed into the epoxy resin to carry out this experimental study. Two sets, one of CTBN pure epoxy, EC1, EC2, EC3, EC4, EC5, and the other of ETBN pure epoxy, EE1, EE2, EE3, EE4, EE5, with formulations of 0, 1, 2.5, 5, 10, 15 wt. % were made, as described in **Table 6**. Four samples of each formulation are made, and the average values are taken into consideration for optimization. The fabrication of toughened epoxy resin samples includes three steps, as represented in the **Figure 4**. These steps are described in detail in the following section.

epoxy resins and also of the other polymers that are used as matrix systems. This makes them ideal to be used in components and structures for sectors like aerospace, automotive, and as a structural adhesive.

**Table 5** Physical and chemical properties of Toughener I-CTBN[47], Toughener II - ETBN [48].

SN	Property	Value
CTBN		
1.	Viscosity at 25 °C	5,00,000 – 10,00,000 mPa*s
2.	Density at 25 °C	0.94 - 0.98 g/cm <sup>3</sup>
3.	Acrylonitrile content	24-28 %
4.	Carboxyl content	30-38 %
ETBN		
1.	Consistency	Thick
2.	Density at 25 °C	0.93 - 0.97 g/cm <sup>3</sup>
3.	Epoxy Value	2.8 – 3.1 Eq. / Kg



**Figure 3.** Pictorial Representation of materials used in this study, (a) Epoxy Resin CY 230, HARDENER HY 951, (c) TOUGHENER I - CTBN, (d) TOUGHENER II - ETBN

### 2.2.1 Synthesis of Reactive Rubber and Epoxy Blends

As shown in **Figure 4** (stage I), The required quantity of respective toughener CTBN or ETBN was added to the epoxy resin at a constant rate and continuously stirred with the help of a spatula. This suspension is kept again on the magnetic stirrer for 10 minutes to ensure proper mixing and achieve a homogeneous suspension. Further in step three, the suspension is kept in a desiccator for 30 minutes with the motive to remove all the bubbles encountered.

### 2.2.2 Incorporation of Hardener to Initiate Curing

As shown in **Figure 4** (stage II), The hardener HY-951 is added to the toughened epoxy in a ratio of 100:10 as suggested by the manufacturer. After adding hardener to the epoxy, the reaction begins, and curing starts, which will make a solid and durable sample.

### 2.2.3 Preparation of Toughened Epoxy Samples

So, in Figure 4, in stage III, suspension is poured into the metal mould of specified dimensions. Epoxy CY-230/1 is a low-viscosity resin that cures at room temperature for 24-48 hours and then oven curing at 60 °C for 5-8 hours. After cooling, the final cured samples are removed with the help of a needle and hammer.

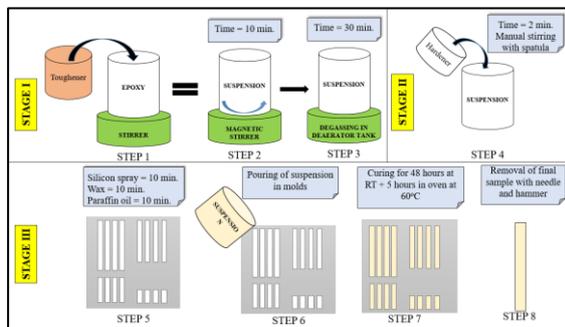


Figure 4. Procedure of fabrication of toughened epoxies.

### 3. Characterization of Toughened Epoxy Blends

#### 3.1 Rheological Characterization

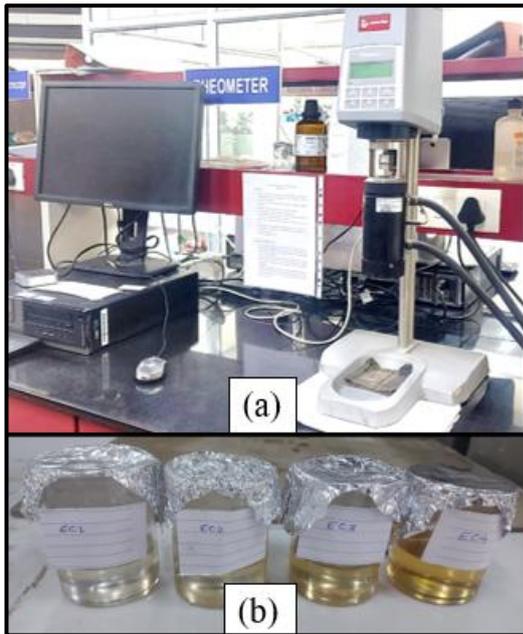
Rheological characterization of CTBN and ETBN toughened epoxy resins involves studying the flow and deformation behaviour of these materials during mixing and moulding processes. It determines the influence of toughening agents on epoxy resin with respect to its peak viscosity and critical shear rate. This characterization was investigated using a rotational rheometer in UPES, details of which are given in

**Table 7.** The measurements were made following ISO 3219-2 standards. Such a type of rheometer is useful for polymeric materials having high viscosity suspended with particles. A concentric cylinder having a cup and bob type of geometry is used for this study. The suspension is being loaded into the cup to the specified level to ensure the immersion of the bob. The temperature is being set and changed after completion of each test. The software displays the result in the form of properties and graphs on the computer attached to the rheometer. After completion of the test, the cleaning of all the parts with solvent is performed rigorously to avoid any malfunction of the rheometer. **Figure 5(a)**

illustrates the experimental set-up of rheological characterization, which is used to investigate properties like viscosity and critical shear stress of the CTBN/ ETBN toughened epoxy polymer system. The rotational rheometer is connected to a computer for data acquisition and analysis. This setup enables the precise control of shear rate and measurement of rheological properties. **Figure 5(b)** represents the suspensions of CTBN-epoxy having varied concentrations, prepared in the UPES laboratory. These suspensions were stored in glass beakers and are sealed with aluminium foil to avoid any contamination. These suspensions are further used to test the flow properties of CTBN, ETBN-modified epoxy.

**Table 6.** Sample Specification

Sr. No.	Sample Code	Investigated Parameter	Toughener With Wt. %	Resin/ Hardener	Curing Cycle
1.	Pure Epoxy	$\mu$ , CSS, T10%, T50%, Tmax, UTS, UFS, IS, TM	0% CTBN	Araldite CY 230-1/ Aradur HY 951	48 hours @RT + 5 hours at 60 deg. in oven
2.	EC1	$\mu$ , CSS, T10%, T50%, Tmax, UTS, UFS, IS, TM	1% CTBN	Araldite CY 230-1/ Aradur HY 951	48 hours @RT + 5 hours at 60 deg. in oven
3.	EC2	$\mu$ , CSS, T10%, T50%, Tmax, UTS, UFS, IS, TM	2.5% CTBN	Araldite CY 230-1/ Aradur HY 951	48 hours @RT + 5 hours at 60 deg. in oven
4.	EC3	$\mu$ , CSS, T10%, T50%, Tmax, UTS, UFS, IS, TM	5% CTBN	Araldite CY 230-1/ Aradur HY 951	48 hours @RT + 5 hours at 60 deg. in oven
5.	EC4	$\mu$ , CSS, T10%, T50%, Tmax, UTS, UFS, IS, TM	10% CTBN	Araldite CY 230-1/ Aradur HY 951	48 hours @RT + 5 hours at 60 deg. in oven
6.	EC5	$\mu$ , CSS, T10%, T50%, Tmax, UTS, UFS, IS, TM	15% CTBN	Araldite CY 230-1/ Aradur HY 951	48 hours @RT + 5 hours at 60 deg. in oven
7.	EE1	$\mu$ , CSS, T10%, T50%, Tmax, UTS, UFS, IS, TM	1% ETBN	Araldite CY 230-1/ Aradur HY 951	48 hours @RT + 5 hours at 60 deg. in oven
8.	EE2	$\mu$ , CSS, T10%, T50%, Tmax, UTS, UFS, IS, TM	2.5% ETBN	Araldite CY 230-1/ Aradur HY 951	48 hours @RT + 5 hours at 60 deg. in oven
9.	EE3	$\mu$ , CSS, T10%, T50%, Tmax, UTS, UFS, IS, TM	5% ETBN	Araldite CY 230-1/ Aradur HY 951	48 hours @RT + 5 hours at 60 deg. in oven
10.	EE4	$\mu$ , CSS, T10%, T50%, Tmax, UTS, UFS, IS, TM	10% ETBN	Araldite CY 230-1/ Aradur HY 951	48 hours @RT + 5 hours at 60 deg. in oven
11.	EE5	$\mu$ , CSS, T10%, T50%, Tmax, UTS, UFS, IS, TM	15% ETBN	Araldite CY 230-1/ Aradur HY 951	48 hours @RT + 5 hours at 60 deg. in oven



**Figure 5.** Rheological Characterization setup and prepared samples, (a) Rotation Rheometer, (b) Prepared Toughened-Epoxy Suspensions

### 3.2 Thermal Characterization

Thermal Gravimetric Analysis (TGA) of CTBN, ETBN toughened epoxy resin CY230-1 is performed to evaluate the thermal stability and composition of samples by measuring weight loss as a function of temperature. TGA provides insights into degradation behaviour, phase separation, and the impact of elastomer modification.

The thermogravimetric analysis of CTBN and ETBN-toughened epoxy resin samples was carried out in accordance with the ISO 11358:1 standard using a TGA 4000 series instrument. For each test, small sections of cured epoxy resin, representing all ratios of CTBN and ETBN toughened epoxy resin, were carefully cut to obtain specimens in the range of 5-10 mg. These prepared samples were then placed into an inert crucible to avoid any external interaction during heating. The analysis was conducted under a controlled heating program, where the temperature was increased from ambient conditions up to 800 °C. at a constant heating rate of 10 °C/ min. Throughout the heating cycle, the instrument is continuously monitored and records the changes in mass of the sample as a function of time and temperature. The output data recorded the residual mass (mg), corresponding temperature (°C), and the derivative weight loss rate (mg/min). Using the collected data, both TGA and DTG curves were plotted. These graphical representations provided insight into the thermal stability, decomposition behaviour, and degradation stages of the epoxy resin systems. The obtained

results were subsequently utilized for detailed comparison and analysis of the influence of incorporating CTBN and ETBN into epoxy resins on thermal properties.

### 3.3 Mechanical Characterization

Mechanical testing, including tensile test, three-point bending test, and impact test of cured toughened epoxies using two different tougheners were carried out. Four samples of each toughener and each ratio were made, and tests were conducted. The results were recorded and used to compare the mechanical properties of both ETBN and CTBN. This study will give the best suitable toughener with selected epoxy CY 230-1. Also, this study will give the optimum concentration of liquid-based rubber toughener, which will give the best performance characteristics. For statistical purposes, a total of four samples of each toughener of each weight percent are carried out at room temperature. The average value of four specimen was taken for final analysis.

Tensile test of toughened epoxies was carried out to study the ultimate tensile strength. **Figure 6(a)** The cured samples of toughened epoxies with different weight content are removed from the metal moulds, and the edges of the samples are finished with sandpaper. The rectangular-shaped tensile test samples of dimension 150 mm x 15 mm x 4 mm with an aspect ratio of 10:1 are made according to ASTM 3039 standards, as shown in the **Figure 6(b)** The tensile tests were carried out on a universal testing machine (50 T capacity) with a crosshead speed of 1mm/min. Four samples were subjected to tensile tests, and their values were recorded. The failed sample is represented in **Figure 6(c)**.

The equation to calculate the ultimate tensile strength of toughened epoxy samples is given below, [49]

Equation 1.

$$S_t = \frac{P_{max}}{A_o}$$

The flexural properties of liquid rubber toughened epoxy polymers are influenced by a combination of factors like material selection, their composition, processing conditions, curing cycles, and environmental conditions. Like, epoxies are prone to uptake moisture, which degrades the mechanical properties and interfacial adhesion. Such an environment should be avoided while working with epoxy resins. The amount of liquid rubber added to the epoxy matrix significantly affects flexural strength and modulus. [50]. Low concentration enhances

toughness without compromising rigidity, while excessive amount reduces stiffness and strength. [51] [52]. The specific type of reactive liquid rubber, like CTBN or ETBN, influences the compatibility with epoxy resin. In this current study, a detailed analysis and comparison of CTBN and ETBN toughened epoxy resin is done, which results in the conclusion of the best suitable toughener for the CY-230/1 grade of epoxy resin. Also, the optimum concentration (in wt. %) of the best suitable toughener is concluded based on the results obtained from experiments.

A three-point bending test of the ETBN, CTBN toughened epoxy is carried out to study the ultimate flexural strength. This test was carried out using a universal testing machine. **Figure 6(d)**. The rectangular-shaped three-point bending test samples of dimension 125 mm x 13 mm x 4 mm with a supporting span of 64 mm, which was 16 times the thickness, were made according to ASTM D790 standards, as shown in the **Figure 6Error! Reference source not found. (e)Error! Reference source not found.** Ultimate flexural strength of the samples was calculated by the following. Equation 2.

Equation 2. The equation to calculate the ultimate flexural strength of toughened epoxy samples is given below, [53]

$$S_f = \frac{3FL}{2bt^2}$$

where F is the load applied in N, L is the span length in mm, b is the width in mm, and t is the thickness in mm of the specimen.

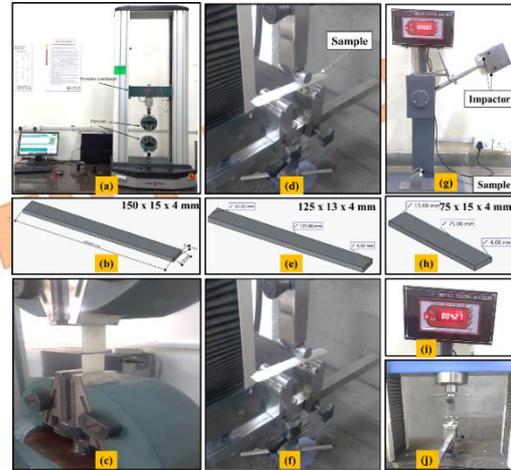
Ultimate flexural strength of toughened epoxy samples was monitored, which signifies the maximum stress it can withstand before breaking when subjected to flexural load. The sample is supported from both ends, and the load is applied at the middle of the sample, as shown in **Figure 6Error! Reference source not found. (j)**.

Un-notched Charpy impact test of ETBN, CTBN toughened epoxy is carried out to study the toughness of the material. The test was conducted on a 50 Joules capacity impact testing machine, Shambhu Nath and Sons, Delhi-made. Impact energy in joules is recorded and further used to calculate the impact strength of the specimen. The rectangular-shaped impact test samples of dimension 75 mm x 15 mm x 4 mm according to test standard ASTM 4812, as shown in the **Figure 6Error! Reference source not found. (h)**. The impact strength of toughened epoxy samples was further calculated using the following Equation 3.

Equation 3. The Equation to calculate the impact strength of toughened epoxy samples. [54],

$$S_i = \frac{U_{abs}}{A}$$

where  $U_{abs}$  is energy absorbed in joules, and A is the cross-sectional area in  $m^2$  of the test specimen.



**Figure 6.** Mechanical Characterization Set-Up and Specimen Details for Tensile, Flexural, and Impact Test of Toughened Epoxy Polymer

**Figure 6–** Tensile test: (a) UTM setup, (b) Specimen, (c) Failed Sample,

3-point bending test: (d) Setup, (e) Specimen, (f) and (j) Sample positioning,

Impact test: (g) Setup, (h) Specimen, (i) Readings observed

## 4. Results and Discussions

### 4.1 Rheological Characterization

Rheological characterization is essential for understanding the flow behaviour and viscoelastic properties of toughened epoxy resins. It provides insights into the influence of CTBN and ETBN on the curing process, viscosity, and overall processability of epoxy systems.

**Table 7.** Details of Rheological Characterization

Characterization	Rheology
Instrument	Rotation Rheometer
MAKE	Anton Paar RheolabQC
Standard Followed	ISO 3219-2
Properties Analysed	Peak Viscosity, Critical Shear Stress, Temperature
Measuring points taken	1 to 100
Controlled Shear Rate	1 to 1000 1/ sec

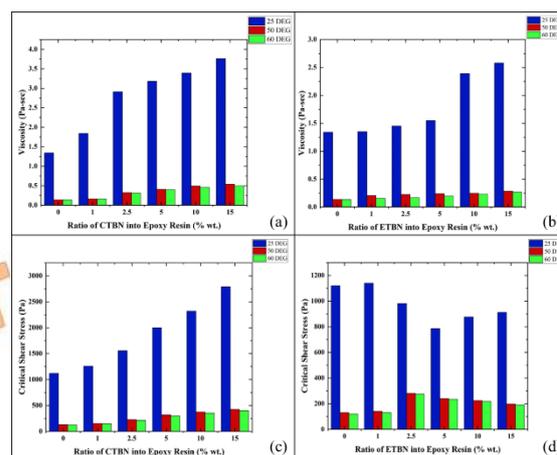
#### 4.1.1 CTBN-EPOXY blends

The graphs (a), (b) in the below **Figure 7** represents peak viscosity (in Pa-sec) vs. RLR content (in wt. %). It shows the effect of different toughener content (0, 1%, 2.5%, 5%, 10%, 15%) on the peak viscosity of epoxy resin CY 230-1 at three temperatures; 25°C (blue), 50°C (red), 60°C (green). As shown in **Figure 7** (a), (b) 25°C, peak viscosity increases significantly with increasing CTBN, ETBN content. This trend indicates that the addition of CTBN, ETBN leads to higher resistance to flow at lower temperature, likely due to the formation of a more complex molecular network or increased molecular interactions. At higher temperatures (50°C & 60°C), viscosity value decreases for all RLR content levels. This is expected because increasing temperature reduces molecular friction, viscosity and thereby enhances the mobility of polymer chains. The difference between viscosities at 25°C and 50°C/ 60°C is more pronounced at higher CTBN content levels as compared to ETBN levels, which suggests that the system is more temperature-sensitive when modified with CTBN whereas ETBN toughened epoxies are less prone to get viscous. At 25°C, viscosity seems to plateau beyond 10 wt. % for ETBN. This could indicate a saturation point where further ETBN addition does not significantly increase molecular interaction which affects viscosity. A similar trend is observed at 50°C/ 60°C although the absolute viscosity values are very low. In graph (c) of **Figure 7**, there is a significant increase in critical shear stress with increasing CTBN content at 25 deg C and graph (d) of **Figure 7**, there is no significant increase in critical shear stress after 1 wt. % of ETBN. Higher critical shear stress indicates stronger interfacial bonding between epoxy resin and CTBN, also it indicates material's capacity to withstand greater mechanical loads without failure. Higher value of critical shear stress also suggests better resistance to crack propagation. RLR modified epoxies help in absorbing energy during mechanical impacts which in-turn reduces

brittleness. Both the graphs (c) and (d) shows that at higher temperatures 50°C and 60°C, critical shear stress decreases drastically which means the material becomes weak at higher temperatures.

#### 4.1.2 ETBN-EPOXY Blends

The graph (b) of **Figure 7** **Error! Reference source not found.** shows the viscosity (in Pa-sec) of a mixture of ETBN and Epoxy Resin at different temperatures (25°C, 50°C & 60°C). The viscosity is highest at 25°C (blue bar) and significantly lower at high temperatures. Viscosity decreases with an increase in temperature, indicating a typical behaviour of thermosetting resin. At 25°C, viscosity increases as the ETBN content increases, particularly after 5 wt. %. At higher temperatures viscosity remains relatively low, and does not show a steep increase, even with higher ETBN content. The effect of ETBN concentration is more pronounced at lower temperatures. The rapid increase in viscosity at 25°C suggests that ETBN has a significant thickening effect at room temperature. However, at elevated temperatures, the mixture maintains lower viscosity, which could be beneficial for processing and application. **Figure 7**(c), (d) graphs provide a comparison of the critical shear stress (in Pa) as a function of CTBN and ETBN content in an epoxy system, observed at three temperatures 25°C (blue), 50°C (red), 60°C (green). (b) Shows a steep increase in critical shear stress with increasing content, reflecting stronger interactions and phase separation behaviour in the resin.



**Figure 7.** (a) Effect of CTBN content on Peak Viscosity of Epoxy at different Temperatures, (b) Effect of ETBN content on Peak Viscosity of Epoxy at different Temperatures, (c) Effect of CTBN content on critical shear stress at different temperatures, (d) Effect of ETBN content on critical shear stress at different temperatures.

#### 4.1.3 Comparison of CTBN-Epoxy and ETBN-Epoxy Blends

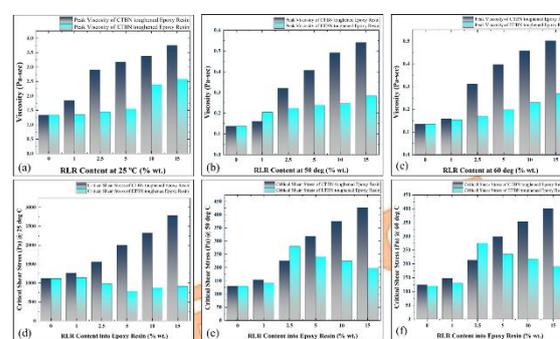
The graphs (a), (b), (c) in **Figure 8** compares the peak viscosity of CTBN-toughened and ETBN-toughened epoxy resins at different temperatures (25 °C, 50 °C, 60 °C), RLR/toughener content levels. As the toughener content increases, the viscosity of both the blends increases at all temperatures. CTBN-toughened epoxy resins show consistently higher viscosity than ETBN-toughened epoxy resins at all RLR content levels and at all temperatures. **Figure 8** (a) gives the comparison at 25 °C. CTBN-toughened epoxy resins exhibit a steeper increase in viscosity, while ETBN-toughened epoxy resins also increase viscosity but at a lower rate. Similar trends are observed at temperatures of 50 °C and 60 °C in **Figure 8** (b), (c). Lower viscosity of ETBN-epoxy blend at all temperatures and all RLR content levels will lead to easier processing, making it more suitable for applications requiring better flow, such as casting, coating, and impregnation in composites. It reduces the risk of trapped air bubbles and incomplete Mold filling. Also, it can be observed that ETBN increases viscosity in a gradual manner. This controlled increase ensures predictable behaviour, which is beneficial for industries where maintaining a consistent flow profile is essential. The ETBN-epoxy blend possesses lower viscosity as compared to the CTBN-epoxy blend. Because of its lower viscosity, the epoxy-ETBN blend could lead to better dispersion of fillers or reinforcements within the resin. This is beneficial in composite manufacturing, where uniformity of the matrix is critical for mechanical performance. Since ETBN still improves viscosity as compared to the 0% RLR, it may provide toughness enhancements without making the resin too thick. If toughness is comparable to CTBN while keeping viscosity lower, ETBN could offer a better balance between toughness and processability. Lower viscosity material often requires less energy for mixing and processing, reducing manufacturing costs.

It can be concluded that if the application requires easy processing, better flow, and more efficient dispersion of fillers, then ETBN is a better choice. While CTBN provides higher viscosity, which could be useful for structural applications. ETBN balances toughness with viscosity, herewith balancing processability, making it ideal for coatings, adhesives, and composite resins where ease of handling is crucial.

The (d) (e) (f) graphs in **Figure 8** Compare the critical shear stress (Pa) of CTBN-toughened and ETBN-toughened epoxy resins at different temperatures (25 °C, 50 °C, 60 °C), RLR/toughener content levels. It can be concluded that CTBN provides significantly better shear strength

at all temperatures, especially at higher contents. This is due to its effective energy dissipation through cavitation and plastic deformation. ETBN performs well at lower temperatures and moderate ETBN content. Its superior interfacial adhesion results in localized stress transfer, enhancing shear resistance at lower ETBN content.

For applications requiring high shear strength across a temperature range higher ratio of CTBN in epoxy resin is preferable. However, for better thermal resistance and moderate performance, 1 to 2.5 wt. % of ETBN is suggested. This study suggests the toughener that can be used, between CTBN and ETBN, based on the basis of operating temperature.



**Figure 8.** Comparison of CTBN toughened Epoxy and ETBN toughened Epoxy based on Rheological properties.

## 4.2 TGA Analysis of CTBN Toughened epoxy resin and ETBN Toughened epoxy resin

Thermo-gravimetric analysis (TGA) is a widely used thermal analysis technique to evaluate the thermal stability and decomposition behaviour of polymer materials. In this study, TGA is employed to investigate the thermal degradation of CTBN-toughened epoxy resin and ETBN-toughened epoxy resin. Understanding the thermal stability of these toughened epoxy systems is essential for their application in high-temperature environments, particularly in aerospace, automotive, and industrial sectors.

### 4.2.1 CTBN-EPOXY blends:

**Figure 9** (a) shows the TGA curve showing the weight loss of different samples of CTBN toughened epoxies as a function of temperature. All curves show a sharp drop in weight at around 300-400 °C, indicating thermal degradation. The final residual weight is maximum for EC3 suspension containing 5 wt. % CTBN into epoxy resin, this content leads to higher char yield at the end of degradation, indicating improved thermal resistance. The neat epoxy suspension (pure epoxy; black curve) shows the lowest thermal stability. The suspension with increasing CTBN

content till 5 wt. % (EC1, red; EC2, blue; EC3, green) shows increasing thermal conductivity, whereas the suspension with 10 wt. % and 15 wt. % (EC4, purple; EC5, brown) CTBN have lower thermal stability as compared to EC3. So, CTBN acts as a toughening agent, improving the thermal stability of the epoxy composites. This is likely due to the barrier effect of CTBN, which slows down the thermal decomposition and enhances char formation. Materials that leave behind more char typically have better resistance to heat and fire, as the char layer acts as a protective barrier, slowing further decomposition [55] [56]. **Table 8** gives the values of T10%<sup>o</sup>C, T 50%<sup>o</sup>C, and Tmax <sup>o</sup>C. T10%<sup>o</sup>C and T50% <sup>o</sup>C is the temperatures at which 10% and 50% weight loss occurs. Higher T10%<sup>o</sup>C and T50%<sup>o</sup>C value indicates better thermal stability, as the material resists degradation at higher temperatures. Lower value of T10% <sup>o</sup>C suggests poor thermal stability, which means the decomposition starts earlier. EC3 suspension has the highest T10%<sup>o</sup>C (245.79 °C) and T50%<sup>o</sup>C (380.82 °C), which indicates that it is the most thermally stable suspension among all the other samples. The probable reason is that it possesses a better composition, higher cross-linking, and strong bonding, which delays the initial decomposition. T10%<sup>o</sup>C of EC5 is the lowest, which means it degrades at a much lower temperature. EC5 possesses higher volatile content and a weaker structure, making it more degradable at lower temperatures.

**Table 8.** Thermal Stability of CTBN toughened Epoxies

Sample Name	T10% <sup>o</sup> C	T50% <sup>o</sup> C	Tmax. <sup>o</sup> C
Pure Epoxy	235.41	370.88	368.25
EC1	237.42	375.21	373.34
EC2	238.94	380.81	385.53
EC3	245.79	380.82	373.03
EC4	235.81	378.01	367.93
EC5	191.29	372.16	370.98

#### 4.2.2 ETBN-EPOXY blends:

The below **Figure 9** shows thermos-gravimetric analysis (TGA) graph, presenting the thermal stability of epoxy resins modified with various ETBN content, ranging from 0 to 15%. Weight % describes the decomposition of epoxy resin as the temperature increases. There is no noticeable trend that can be observed. All the curves show a sharp drop in weight at around 300-400 <sup>o</sup>C, indicating thermal degradation. The final residual weight is maximum for 1wt. % suspension (EE1, red). The suspensions with 2.5 wt. % and 15 wt. % ETBN (EE2, blue; EE5, brown) content into epoxy possess lowest thermal stability. This is

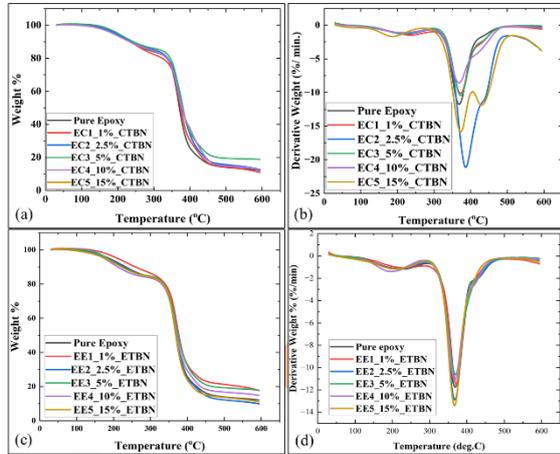
related to an insufficient barrier effect, slowing down heat and mass transfer during decomposition. There may be improper dispersion of ETBN into the epoxy of EE2 suspension, because of which the effective protective layer could not form, and the epoxy tends to degrade faster. The suspensions with 1 wt. %, 5 wt. % and 10 wt. % ETBN (EE1, red; EE3, green; EE4, purple) possesses good thermal stability as compared to the neat epoxy. So, EE1 suspension containing 1 wt. % ETBN is capable of improving the thermal stability of epoxy. **Table 9** gives the values of T10% <sup>o</sup>C, T50% <sup>o</sup>C, Tmax <sup>o</sup>C. It can be observed that the values for EE1 samples are maximum, making it the most thermally stable suspension, as compared to the other suspensions containing a higher content of ETBN in epoxies.

**Table 9.** Thermal Stability of ETBN toughened Epoxies

Sample Name	T10% <sup>o</sup> C	T50% <sup>o</sup> C	Tmax <sup>o</sup> C
Pure Epoxy	231.63	370.88	368.06
EE1	260.02	377.30	371.76
EE2	228.91	372.97	367.15
EE3	243.04	380.42	367.45
EE4	223.41	374.86	365.60
EE5	235.35	372.06	366.82

The Derivative Thermogravimetric (DTG) curves shown in **Figure 9** (c) and (d) depict the rate of weight loss as a function of temperature for the CTBN and ETBN modified epoxy system. The peak of these graphs gives the value of maximum decomposition temperature (T<sub>max</sub> <sup>o</sup>C), the value of which is given in Tables 8 and **Table 9**. All samples exhibit a single major degradation peak, indicating that the thermal degradation occurs predominantly in one step associated with the breakdown of the epoxy matrix. When graph (c) is observed, the peak shifts slightly towards the lower values of temperature with increasing CTBN content. This suggests that adding a higher concentration of CTBN into the epoxy resin reduces the thermal stability because of the lower thermal resistance of CTBN. Also, it can be noticed that the intensity of the degradation peak increases with higher CTBN content, suggesting an enhanced mass loss rate. On the contrary, when graph (d) is observed, ETBN modified epoxy resin displays more stable behaviour. These possess only minor shifts in maximum degradation temperature, even at the higher concentration of ETBN. This indicates better thermal stability of ETBN as compared to CTBN. Overall, from DTG curves, it can be concluded that both CTBN and ETBN influence the

decomposition behaviour of the epoxy system, with ETBN showing better thermal stability while maintaining a consistent degradation profile. Sample containing 1 wt. % of ETBN into epoxy shows the excellent performance as it has the highest value of  $T_{max}$  °C.

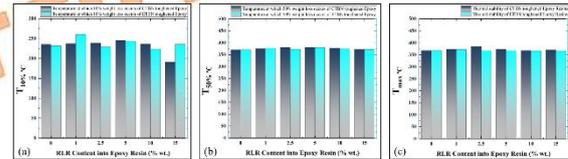


**Figure 9.** (a) Thermogravimetric analysis (TGA) curves of CTBN toughened Epoxy Resins with varying CTBN content, (b) Thermogravimetric analysis (TGA) curves of ETBN toughened Epoxy Resins with varying ETBN content, (c) Derivative Thermogravimetric Curve (DTG) of ETBN toughened Epoxy Resins with varying ETBN content.

#### 4.2.3 Comparison of CTBN-toughened Epoxy Resins and ETBN-toughened Epoxy Resins for Thermal Stability:

Figure 10 presents a comparative analysis of thermal properties of CTBN and ETBN toughened epoxy resin samples at different concentrations of these Reactive Liquid Rubber (RLR) as tougheners. The comparisons are made using three parameters.  $T_{10\%}$ , temperature at which 10% weight loss occurs,  $T_{50\%}$ , temperature at which 50% weight loss occurs, and  $T_{max}$ , maximum degradation temperature, typically representing the peak thermal decomposition temperature. As per the graph (a) of the Figure, the ETBN-toughened epoxy sample showed higher  $T_{10\%}$ , compared to CTBN at almost all concentrations, indicating better thermal stability. The maximum  $T_{10\%}$  is observed of EE2 sample with 2.5 wt. % of ETBN, reaching approximately 260 °C. CTBN follows a similar trend but at slightly lower temperatures. This suggests that ETBN provides lower resistance to initial thermal degradation. At 15 wt. %, both CTBN and ETBN toughened epoxy systems experience a decline in this temperature, which may be due to a phase separation mechanism, agglomeration of particles, or reduced cross-linking density of epoxy, hardener, and toughener materials. As per graph (b) of Figure 10, both the systems exhibit similar  $T_{50\%}$  temperatures, having their values ranging

between 370°C to 380°C. ETBN displays better stability at higher loadings, and the differences are hardly noticeable compared to the values of T10%. Comparable results of thermal resistance offered can be observed by both the tougheners at mid-level.  $T_{max}$  values also follow a consistent pattern across all the loadings, with ETBN values displaying slightly higher values as compared to CTBN, as observed in graph (c) of Figure 10. Only minor fluctuations can be observed across all the concentrations, and it can be said that the thermal stability is fairly stable.



**Figure 10.** Comparison of CTBN toughened Epoxy and ETBN toughened Epoxy based on Thermal properties.

### 4.3 Mechanical Characterization

Mechanical characterization is very crucial for determining the structural performance of epoxy resins toughened with RLRs. In this section, mechanical properties of toughened epoxy are calculated and analyzed to find mechanical properties. This section focuses on tensile, flexural, and impact properties of CTBN and ETBN-toughened epoxy samples to achieve an understanding of their suitability for various applications.

#### 4.3.1 CTBN-EPOXY blends:

Figure 11 (a) and (c) shows the tensile properties of CTBN toughened epoxy resin. Tensile modulus is calculated from the offset method. It can be observed that initially, there is a sharp drop in Ultimate Tensile Strength (UTS) at 1 wt. %, which indicates poor stress transfer may be likely due to improper rubber particle dispersion into the epoxy resin. The UTS value is recovered and reaches the peak value at 5 wt. % of CTBN, suggesting the occurrence of the phase separation phenomenon, ensuring better performance and energy dissipation. After 5 wt. %, UTS declines again, particularly 15 wt. %, which may be due to clustering or rubber particles and weak interfacial bonding among them. The tensile modulus remains particularly stable till 2.5 wt. % of CTBN, then it peaks at 5 wt. %, indicating enhanced stiffness.

Beyond 5 wt. %, the modulus drops, possibly due to excessive rubber domains leading to matrix softening. At 5 wt. %, the error bars are smaller for both properties, showing better uniformity in mechanical properties. So, this can be interpreted from both the graphs that 5 wt. % CTBN suggests

a balanced microstructure with efficient stress transfer and crack bridging. Beyond this rubber

agglomeration leads to a reduction in both strength and modulus.

**Table 10.** Maximum Values of CTBN Toughened Epoxy Resin

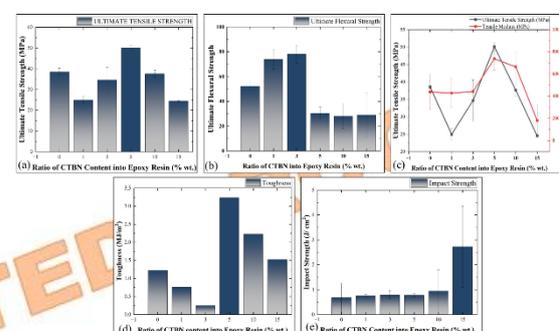
PROPERTY	TEST METHOD	SAMPLE ID	AVERAGE VALUE	UNIT
Ultimate tensile strength	ASTM D 3930	EC3	50.060	MPa
Tensile modulus	ASTM D 3930	EC3	737.075	MPa
Toughness		EC3	3.235	MJ/ m <sup>3</sup>
Ultimate Flexural Strength	ASTM D790	EC2	78.08	MPa
Impact strength	ASTM 4812	EC5	2.728	J/ cm <sup>2</sup>

Ultimate Flexural Strength (UFS) is a critical mechanical property that is important for structural integrity, where components are subjected to bending loads, and durability, where in cyclic loading environments occurring repeated bending plays a huge role. **Figure 11 (c)**, shows UFS of CTBN toughened epoxy resin. The UFS increases significantly with CTBN addition till 2.5 wt. %. This indicates effective toughening due to improved cracked bridging and energy dissipation. At 5 wt. % and beyond, the UFS drops considerably. This may be due to over-toughening caused by the formation of a large rubber domain. Excess rubber particles act as stress concentrators, leading to poor stress transfer and premature failure under bending loads.

**Figure 11(d)** shows the toughness in (MJ/m<sup>3</sup>) of CTBN toughened epoxy resin. The toughness is calculated from the area under the stress-strain graph till the fracture point. Initially, there is a significant decrease in toughness from 0 to 2.5 wt. % CTBN. The low toughness value could be the cause of the poor phase separation phenomenon, or it may be due to insufficient rubber domain formation, which leads to ineffective crack deflection. Among all the samples, EC3 samples having 5 wt.% of CTBN possess the highest value of toughness, which indicates optimal rubber particle dispersion and effective energy dissipation. The CTBN particles act like efficient stress absorbers, which dissipate and distribute mechanical stress to prevent damage or failure, and also, CTBN enhances crack growth resistance. Beyond 5 wt. % CTBN, toughness value decreases, but it is more compared to the neat epoxy resin.

**Figure 11(e)**, It can be observed that Impact strength remains relatively low and stable up to 10 wt. % CTBN. The toughening mechanisms, such as cavitation or shear yielding, are not fully activated. At 15 wt. % CTBN, the strength dramatically increases, which suggests higher CTBN loadings into epoxy resins, promoting better crack deflection and energy dissipation.

When impact properties are the primary requirement of the application, 15 wt. % CTBN is beneficial. **Table 10** summarizes key mechanical properties of CTBN toughened epoxy samples. These matrices will be beneficial for the researchers working in the same field.



**Figure 11.** Graphical Representation of Mechanical Properties of CTBN-toughened Epoxy Resin.

**Figure 11:** (a) Ultimate Tensile Strength vs CTBN content, (b) Ultimate Flexural Strength vs CTBN content, (c) Ultimate Tensile Strength and Tensile Modulus vs CTBN content, (d) Toughness vs CTBN content, (e) Impact Strength vs CTBN content.

#### 4.3.2 ETBN-Epoxy Blends:

**Figure 13(a)** and **(c)** illustrate the relationship between the ratio of ETBN content in epoxy resin (in weight percentage) and ultimate tensile strength (in MPa) and Tensile Modulus (MPa). UTS peaks at 2.5 wt. % ETBN and tensile modulus peaks at 1 wt. % ETBN. Both these properties decline after 5 wt. % ETBN.

The modulus, particularly, drops sharply at 10 wt. % ETBN, indicating poor structural rigidity at higher rubber contents. This is likely due to phase separation and the formation of rubber-rich domains that reduce crosslink density. However, all the ETBN loadings are capable of enhancing the tensile properties when compared to the properties of neat epoxy samples. But the optimal concentration of ETBN will be considered as 2.5% as the value of Tensile Modulus is at its

second-best value at this concentration, and other properties also show enhancements at this concentration. **Figure 13(b)** represents the UFS as a function of ETBN loadings into epoxy resin. The highest UFS is observed at 5% ETBN, reaching approximately 70 MPa. This indicates enhanced load-bearing capacity under bending stress at this composition. Improved interfacial bonding and phase separation at this concentration may contribute to the optimal performance. There is a steady rise in UFS from 0 to 5 wt. % ETBN, which suggests initial improvements in flexibility and energy dissipation. Beyond 5 wt. % ETBN, UFS decreases slightly, meaning excessive ETBN results in soft rubber phase agglomeration and reduced load-bearing capacities.

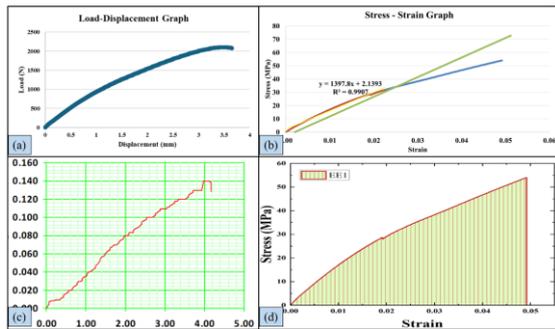
**Figure 13(d)** shows the toughness in (MJ/m<sup>3</sup>) of CTBN toughened epoxy resin. The toughness is calculated from the area under the stress-strain graph till the fracture point. The toughness increases drastically and peaks at 2.5 wt. % ETBN indicates an optimal balance of ductility and energy absorption at this concentration. Although ETBN can be used as a toughener, it enhances the toughness of epoxy matrix systems at all the loadings considered in this study. **Figure 13(e)** gives the impact strength (J/cm<sup>2</sup>) as a function of ETBN loadings. Impact strength increases steadily till 2.5 wt. % ETBN, which means ETBN facilitates crack bridging and cavitation mechanisms that help dissipate impact energy. After 5 wt. % ETBN, the impact strength significantly drops, which indicates rubber particle agglomeration and weak interfacial bonding. The poor load transfer between the epoxy matrix and ETBN reduces the ability of a material to resist impact. **Table 11** summarizes key mechanical properties of ETBN toughened epoxy samples. **Table 12** outlines the optimal CTBN and ETBN content for different mechanical performance goals. Depending upon the applications, ETBN content can be tailored to enhance tensile, flexural, and toughness properties accordingly.

**Figure 12(a)-(b)** illustrates the representative results of the tensile test on toughened epoxy, shown both as a load-displacement graph and a corresponding stress-strain response. The specimen is firmly clamped in the fixtures of the UTM and was tested until complete fracture in accordance with the ASTM 3039 guidelines. During the test, the computer system attached to

the UTM continuously records the load and displacement data, from which the graph (a) of **Figure 12** is plotted. A slight curvature is observed at the toe region, which arises due to grip seating or system compliance. After this, toughened epoxy exhibits a clear linear segment. With increasing strain, a subtle non-linearity is observed, which is due to the yielding of dispersed rubber particles into the epoxy resin, which apparently increases ductility. After the peak load " $P_{max}$ " is achieved, the specimen starts to soften. **Figure 12 (a)** gives the value of Ultimate Force that a sample can resist, which is used in **Error! Reference source not found.** to calculate UTS. This procedure was followed for 4 samples of each concentration, and average values were taken for final comparison and analysis. Besides recording load and displacement, the system is also set to record the stress and strain data throughout the test. This data is used to plot graph (b) of **Figure 12**. The blue curve is plotted from the raw data received from the system. The red curve is plotted till the linear-elastic region. When there is difficulty in noticing a clear linear-elastic region in the stress-strain curve, calculating Tensile Modulus becomes more difficult. The offset method is used to calculate the exact value of tensile modulus in such cases. The new value of stress-strain is calculated by offsetting the value of strain by 0.2%, followed by evaluating the offset stress. The green curve is plotted using the offset stress-strain values. The intersection point of the green and blue curves decides the region of linear elasticity. The red curve is increased till that point, and the trendline is plotted against this red curve. The slope of this trendline gives the value of Tensile Modulus. This procedure is repeated for all the samples, and average values are taken for further comparison and analysis. The flexural test is carried out on the UTM in accordance with ASTM D790 standards. 3-point loading on a simply supported beam is set up to get the flexural strength of toughened epoxy samples. The system synchronized with UTM provides the results in the form of load-displacement data at each point until the sample fails. **Figure 12 (c)** gives the graph plotted with this data. Toughness is the property that is calculated by the area under the stress-strain curve till the fracture point. **Figure 12 (d)** demonstrates the area obtained till the specimen breaks during the tensile test. All these calculations are made using Origin Software.

**Table 11.** Maximum Values of ETBN Toughened Epoxy Resin

Property	Test Method	Sample Id	Average Value	Unit
Ultimate tensile strength	ASTM D 3930	EE2	70.42	MPa
Tensile modulus	ASTM D 3930	EE1	1505.10	MPa
Toughness	-	EE2	3.2	MJ/ m3
Ultimate Flexural Strength	ASTM D790	EE3	66.59	MPa
Impact strength	ASTM 4812	EE2	1.80	J/ cm2

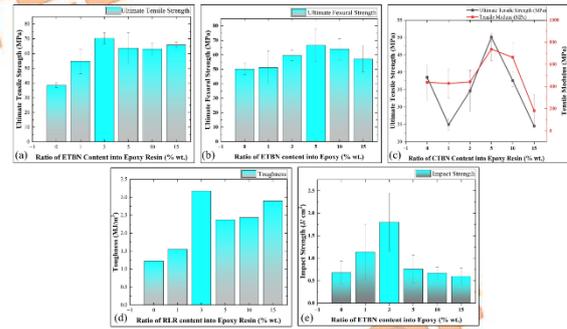


**Figure 12.** (a) Load-Displacement of Tensile Test Specimen and (b) Stress-Strain Response of a Tensile Test Specimen, (c) Load-Displacement of Flexural Test Specimen, (d) Toughness measurement

**Figure 12,** Graph (b): Blue Curve – Stress-Strain Curve from data available from the UTM system,

Red Curve - Stress-Strain Curve till the Linear-Elastic Region,

Green Curve - Stress-Strain Curve obtained from Offset-Method.



**Figure 13.** Graphical Representation of Mechanical Properties of Epoxy-ETBN Blend.

**Figure 13:** (a) Ultimate Tensile Strength vs ETBN content, (b) Ultimate Flexural Strength vs ETBN content, (c) Ultimate Tensile Strength and Tensile Modulus vs ETBN content, (d) Toughness vs ETBN content, (e) Impact Strength vs ETBN content.

UNCORRECTED PROOF

**Table 12.** Engineering Implications of using CTBN and ETBN as Toughening agent into CY 230-1 Epoxy Matrix

Implications	Optimum Weight	Applications
For high- strength components	5 wt. % CTBN	Where high tensile properties are a primary requirement, like reinforced composites, aircraft wings, and fuselage, it has to resist aerodynamic forces.
For structural-load bearing components	2.5 wt. % CTBN	Where high ultimate flexural strength is the primary requirement.
For high impact and fracture resistance	15 wt. % CTBN	Where superior toughness and moderate strength are required.
For High-strength components	2.5 wt. % ETBN	Where high tensile properties are primary requirements, like structural components of aircraft and engine parts which subjected to high stress and vibrations.
Load-bearing structures	5 wt. % ETBN	Where high flexural strength and flexibility are required.
High Energy absorption and impact strength	2.5 wt. % ETBN	Suitable for applications requiring increased toughness, like vibration dampers, protective casings, etc.

#### 4.3.3 Comparison of CTBN toughened Epoxy and ETBN toughened Epoxy on the basis of Mechanical Properties

This bar graph compares the Ultimate Tensile Strength of CTBN and ETBN toughened Epoxy Resins at different contents of these RLR (wt.%). At 1% RLR, ETBN significantly surpasses CTBN, achieving approximately 55 MPa. The superior strength of ETBN toughened epoxy resin samples indicates better phase dispersion and effective stress transfer at low content. At 2.5% RLR, ETBN samples reach a maximum UTS of 70 MPa, while CTBN samples remain lower at 35 MPa. The phase-separated rubber domains in ETBN toughened epoxy might optimize energy dissipation, leading to higher strength. At 5% RLR, ETBN still maintains high UTS around 65 MPa, although a slight decrease is noted as compared to 2.5% RLR. CTBN samples remain steady at 40 MPa, indicating moderate reinforcement. At 10% RLR, ETBN toughened epoxy samples remain at higher UTS as compared to neat epoxy, while CTBN experiences a noticeable drop around 35 MPa. At 15% RLR, CTBN exhibits a significant decline to approximately 25 MPa, likely due to rubber agglomeration and poor stress transfer. ETBN toughened samples demonstrate better UTS across all RLR content levels as compared to CTBN toughened samples. Optimal toughening occurs at around 5% RLR for both the resins, although ETBN shows greater consistency and superior performance at higher loadings. This may be attributed to ETBN's improved phase separation, better interfacial bonding, and higher flexibility in the epoxy matrix.

The graph compares the ultimate flexural strength in MPa of CTBN and ETBN toughened epoxy resins across different RLR content levels.

At low RLR content till 2.5 wt.%, CTBN toughened epoxy samples show a more significant increase in flexural strength, peaking around 2.5 wt.% CTBN with values exceeding 75 MPa. CTBN toughened epoxy samples also increase in UFS but at a slower rate, reaching approximately 60 MPa. When 5 wt.% of these RLRs are added to epoxy resins, it can be observed that ETBN toughened epoxy samples outperform CTBN, achieving UFS close to 65 MPa. CTBN exhibits higher UFS as compared to the ETBN sample, but significantly declines at higher content. So, CTBN can be used as a toughener where high flexibility is required. While ETBN provides consistent flexural strength across a broader range of tougheners, demonstrating better performance in maintaining structural integrity. ETBN's phase separation and interfacial bonding seem more effective in preventing strength loss as compared to CTBN.

The initial impact strength of neat epoxy resin exhibits very low impact strength, around 0.6 J/cm<sup>2</sup>. This shows the brittle nature of the epoxy polymer. When up to 2.5 wt.% of tougheners are incorporated into epoxy resin, ETBN toughened epoxy shows a noticeable increase in the impact strength, as compared to CTBN toughened samples. At 2.5 wt.% ETBN outperforms and reaches 1.8 J/cm<sup>2</sup>, while CTBN remains at below 1 J/cm<sup>2</sup>. This suggests that ETBN induces better rubber particle dispersion and phase separation, enhancing energy absorption.

The graph shows the relationship between CTBN content and the tensile properties of CTBN toughened epoxy resin, focusing on Ultimate Tensile Strength (MPa) and Tensile Modulus (MPa).

When the mechanical properties of toughened cured epoxy samples were compared with the literature available, it can be observed from Table

13 that, this grade of epoxy resin CY-230/1 and tougheners like CTBN and ETBN are capable to enhance toughness of the epoxy resin system by 164% and 159%, respectively, without compromising other properties. As compared to other filler materials from the literature, which are used to enhance mechanical properties, these rubber-based tougheners, CTBN and ETBN, proved their worth in increasing tensile strength (30% and 83%), flexural strength (50% and 32%), tensile modulus (68% and 243%) and impact strength (302% and 166%).

The outcome of this study is to evaluate the most compatible toughener between CTBN and ETBN, which can be incorporated into DGEBA based CY 230-1 epoxy polymer matrix system. The main objective of carrying out this study is to evaluate the rheological, thermal, and mechanical properties of toughened epoxy samples, and compare them to obtain the best properties. Also, the optimum weight of the compatible toughener is evaluated. Table 14 summarizes the values of properties obtained at optimized concentration. This will be helpful for all the young researchers who are working on similar types of domains.

#### *4.3.4 Toughening Mechanics in CTBN and ETBN Toughened Epoxies & Comparative Mechanistic Insights*

When CTBN is blended into epoxy resins, the COOH-terminated functional groups react with the epoxide group of epoxy resins, resulting in the formation of covalent bonds, thereby facilitating phase separation after post-curing. This phase separation results in the formation of discrete rubber-rich domains dispersed within the brittle epoxy matrix [57]. When such modified epoxies are subjected to mechanical loading, these dispersed rubber particles give rise to localized cavitation due to stress concentrations. These resultant voids allow the epoxy matrix to

undergo localized plastic deformation and shear yielding around the cavities [58] [6]. These absorbing and dissipating mechanisms are effective in absorbing mechanical energy and inhibiting crack initiation and propagation. Furthermore, effective interfacial adhesion between the rubber domains and the epoxy matrix improves toughness but significantly affects structural rigidity. ETBN is characterized by epoxy-terminated functional groups and exhibits high reactivity with epoxy groups, which contributes to the formation of covalent bonds like CTBN particles. This facilitates the uniform integration of ETBN into the epoxy matrix, creating a clear and homogeneous dispersion of particles that align with the CTBN particles. This uniform distribution promotes more efficient and effective stress transfer and also ensures improved crack initiation and propagation. When subjected to mechanical loading, ETBN particles withstand elastic deformation and absorb a considerable amount of strain energy. Furthermore, this uniform dispersion reduces particle agglomeration and improves mechanical performance, particularly tensile modulus and ultimate tensile strength.

ETBN and CTBN have different termination chemistry that affects their quality of dispersion and interfacial interaction within the epoxy resin. CTBN enhances the epoxy toughness via cavitation-induced plastic deformation, making it more suitable for applications where a substantial amount of energy absorption is like impact and ballistic loading. Comparatively, ETBN uses enhanced dispersion and interfacial adhesion to achieve notable enhancements in tensile strength and modulus, making it appropriate for applications where there is a requirement for balanced high stiffness and toughness.

**Table 13.** The effect on the mechanical properties of toughened epoxies based on a literature survey:

Ref.	Epoxy resin type	Filler type	Filler content	UTS (MPa)	TM (GPa)	% Increase in UTS	% Increase in TM	UFS (MPa)	Toughness	% Increase in UFS	% Increase in Toughness	IS (J/cm <sup>2</sup> )	% Increase in IS
[59]	Bisphenol A-based E51	Polysulphone (thermoplastic)	15 phr	61.03	1.52	Decreased	Decreased	-	-	-	-	-	-
[60]	DGEBA Epidian 5	Polyurethane	15 wt. %	45	1	125%	Decreased	-	-	-	-	-	-
[61]	EPON 828	Al <sub>2</sub> O <sub>3</sub> nanoparticles	3 wt. %	-	-	-	-	67.0	-	15%	-	-	-
[59]	Bisphenol A-based E51	Polysulphone (thermoplastic)	15 wt. %	-	-	-	-	110.0	-	22.22%	44.68%	-	-
[62]	Quick-mast 105	ZrO <sub>2</sub> nanoparticles	1 wt. %	-	-	-	-	105.7	-	29%	31%	-	-
	Quick-mast 105	Y <sub>2</sub> O <sub>3</sub> nanoparticles	1 wt. %	-	-	-	-	112.1	-	36%	46%	-	-
[63]	Epikote 828 (Bisphenol A-based)	CTBN	5 wt. %	-	-	-	-	-	-	-	-	5	100%
[13]	DGEBA Araldite GY 260	ATBN	12.5 phr	-	-	-	-	-	-	-	-	0.286	236.5% (notched)
	DGEBA Araldite GY 260	ATBN	12.5 phr	-	-	-	-	-	-	-	-	1.426	240.3% (un-notched)
[64]	DGEBA CYD 128	Hyper-branched polymer	10 wt. %	-	-	-	-	-	-	-	-	3.12	20.46%
[60]	DGEBA Epidian 5	Polyurethane	20 wt. %	-	-	-	-	-	-	-	-	0.5	233.3%

Present study	Araldite CY 230-1	CTBN	5 wt. %	50.06	0.737	30%	Decreased by 0.2%		
	Araldite CY 230-1	ETBN	2.5 wt. %	70.42	1.428	82.8%	93.5%		
	Araldite CY 230-1	CTBN	2.5 wt. %				78.08	49.5%	
	Araldite CY 230-1	ETBN	5 wt. %				66.59	32.68%	
	Araldite CY 230-1	CTBN	15 wt. %						2.73 313.6%
	Araldite CY 230-1	ETBN	2.5 wt. %						1.80 261.7%

UNCORRECTED PROOF

UNCORRECTED PROOF

UNCORRECTED PROOF

**Table 14.** Mechanical, thermal, and rheological properties of OPTIMIZED TOUGHENER – ETBN

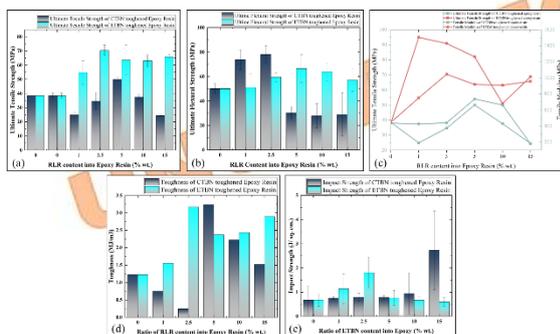
PROPERTY	VALUE	UNIT	% ENHANCEMENT
Optimized Toughener	ETBN		
Optimized Sample ID	EE1		
Optimized Concentration	1 wt.%		
Optimized value of Viscosity @ 25 °C	1.35	Pa-sec	0.75%
Optimized value of Viscosity @ 50 °C	0.205	Pa-sec	49.6%
Optimized value of Viscosity @ 60 °C	0.154	Pa-sec	15%
Optimized value of Critical Shear Stress@ 25 °C	1140	Pa	1.78%
Optimized value of Critical Shear Stress@ 50 °C	141	Pa	8.46%
Optimized value of Critical Shear Stress@ 60 °C	130	Pa	8.33%
Optimized value of T10 °C	260.02	°C	12.25%
Optimized value of T50 °C	377.3	°C	1.70%
Optimized value of Tmax°C	371.76	°C	1%
Optimized the value of Ultimate tensile strength	70.42	MPa	82.8%
Optimized value of Tensile modulus	1.4286	GPa	93.5%
Optimized value of Ultimate Flexural Strength	59.53846	MPa	18.62%
Optimized value of Toughness	3.17113	MJ/ m <sup>3</sup>	160%
Optimized the value of Impact strength	18.02	kJ/ m <sup>2</sup>	166%

#### 4.3.5 Error Analysis:

Figure 11 and Figure 13 contains multiple graphs depicting the effect of CTBN and ETBN content on epoxy resin in terms of ultimate tensile strength, tensile modulus, ultimate flexural strength, toughness, and impact strength. Each graph includes error graphs of standard deviations, indicating the presence of experimental variability. Some data points exhibit larger error bars, which suggest inconsistent material properties due to possible non-uniform dispersion of CTBN and ETBN into epoxy resin, measurement uncertainties in mechanical testing procedures, and batch-to-batch variations in sample preparation. These errors could be minimized with improved processing techniques and controlled testing conditions.

## 5. Application of Toughened Epoxy Polymer Matrix System

Toughened epoxy polymers mean the polymer matrices that have been modified with elastomers. After toughening epoxy polymers with CTBN and ETBN, enriches them with enhanced mechanical and thermal properties, making them ideal for a wide range of demanding applications. The CTBN & ETBN toughened epoxy matrix system can be further reinforced with glass fibres to make toughened GFRP composites. GFRP composites are used to fabricate aircraft components like Radomes. This structure is usually located in the nose of an aircraft to survive weather conditions, bird strikes, rotating antennas, etc. The material of Radomes should be capable to languish electromagnetic signals received or transmitted by the antenna. Antennas are the surfaces in an aircraft that are very crucial for communication and navigation. Radomes are constructed with glass fibre or PTFE-coated composite materials, depending upon the applications, and are made up with various shapes like spherical, planner etc. Toughened GFRP composite material possesses good mechanical properties, which are required for high-performance radome applications. Such mechanical properties include: high strength to withstand high aerodynamic and handling loads; high stiffness to achieve less deformation under loads; high thermal properties to achieve temperature stability at extreme temperatures;



**Figure 14.** Comparison of CTBN toughened Epoxy and ETBN toughened Epoxy on the basis of Mechanical properties.

resistance to abrasion, moisture absorption, and erosion. [65].

## 6. Conclusion and Future Scope of Epoxy Rubber Blend Systems

Epoxy resins modified with ETBN and CTBN have important implications for various industrial applications in the aerospace and automotive sectors. In aerospace, where strength-to-weight ratio and impact resistance are critical, these cured epoxy resins are used to improve resistance to dynamic loads and environmental conditions. Automotive applications, on the other hand, benefit significantly from these epoxy systems in the development of lightweight materials with higher impact, crashworthiness, and fatigue resistance. CTBN and ETBN-modified epoxy resins are suitable for adhesive formulations in electronics, ensuring reliable bonding as well as resistance to thermal cycling and mechanical shocks. The use of recycled rubber offers sustainability benefits: it strictly complies with environmental regulations, promotes waste reduction and efficient use of resources, and minimizes ecological impact. Therefore, these epoxy resins offer economical and durable solutions and meet the stringent standards of the high-performance industry. Further, nano-fillers like nanosilica, alumina, etc., can also be added to these blends to achieve hybrid toughening of nanocomposite materials. Various conclusions derived from the study are given as follows:

- I. For applications requiring ease of flow, higher processing temperatures are recommended, particularly for formulations beyond 5wt % of CTBN and ETBN. CTBN is preferable for applications requiring higher viscosity and structural reinforcement, especially at lower temperatures. ETBN is better suited for high-temperature applications or when low

viscosity is desired, ensuring better flow, easier processing, and reduced energy requirements in manufacturing.

- II. CTBN and ETBN show similar types of results over thermal stability, especially at T<sub>10%</sub>, At T<sub>50%</sub> °C, and T<sub>max</sub> °C CTBN outperforms ETBN. The higher initial degradation temperature (T<sub>10%</sub>) indicates that CTBN and ETBN-toughened epoxy can withstand thermal stress in the early degradation phase. Applications requiring greater thermal resistance, CTBN, and ETBN are the preferred choice, considering their minor fluctuations.
- III. But, whenever higher mechanical properties are the prime demand of the application, ETBN toughened epoxy resin is recommended by this study. ETBN toughened epoxy exhibits superior tensile strength at all RLR content levels when compared to CTBN toughened epoxy resin, because of more effective phase separation, stronger interfacial bonding, and better compatibility with the epoxy matrix. 5 wt. % CTBN is the most effective toughening concentration for achieving the highest tensile strength, modulus, and modulus, ensuring improved mechanical performance, without excessive material softening.
- IV. Based on this study, 1 wt. % ETBN is optimal when high flexibility, durability, and structural integrity are important. ETBN can be used as a toughener, as it enhances all the mechanical properties like tensile strength, modulus, flexural strength, and toughness of epoxy matrix systems at all the loadings considered in this study.

## Nomenclature

*RLR* Reactive Liquid Rubber

*DGEBA* Di-Glycidyl Ether Bisphenol-A

*CTBN* Carboxyl Terminated Butadiene Nitrile

*ETBN* Epoxy Terminated Butadiene Nitrile

*UTS* Ultimate Tensile Strength

*UFS* Ultimate Flexural Strength

*IS* Impact Strength

*T<sub>M</sub>* Tensile Modulus

*T<sub>g</sub>* Glass Transition Temperature

*ILSS* Inter Laminar Shear Strength

*μ* Peak Viscosity

*CSS* Critical Shear Stress

*T<sub>10%</sub>* 10% Decomposition Temperature

*T<sub>50%</sub>* 50% Decomposition Temperature

*T<sub>max</sub>* Maximum Decomposition Temperature

## Acknowledgments

The authors gratefully acknowledge the financial support provided by the Department of Science and Technology (DST), Government of India, under the Teachers Associateship for Research Excellence (TARE) scheme, **Project no: TAR/2022/000309**, for carrying out this research work.

## Funding Statement

Please specify any sources of funding (institutional, private, and corporate financial support) for the work reported in their paper. If no funding has been provided for the research, please state the following: This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

## Conflicts of Interest

The author declares that there is no conflict of interest regarding the publication of this article.

## References

- [1] H. Pulikkalparambil, S. M R, S. Siengchin, and J. Parameswaranpillai, "Introduction to Epoxy Composites," 2021, pp. 1–21. doi: 10.1002/9783527824083.ch1.
- [2] S. M. Harle, "Durability and long-term performance of fiber reinforced polymer (FRP) composites: A review," *Structures*, vol. 60, p. 105881, 2024, doi: <https://doi.org/10.1016/j.istruc.2024.105881>.
- [3] H. Abdellaoui, M. Raji, R. Bouhfid, and A. el kacem Qaiss, "2 - Investigation of the deformation behavior of epoxy-based composite materials," in *Failure Analysis in Biocomposites, Fibre-Reinforced Composites and Hybrid Composites*, M. Jawaid, M. Thariq, and N. Saba, Eds., in Woodhead Publishing Series in Composites Science and Engineering. , Woodhead Publishing, 2019, pp. 29–49. doi: <https://doi.org/10.1016/B978-0-08-102293-1.00002-4>.
- [4] S. Liu, V. S. Chevali, Z. Xu, D. Hui, and H. Wang, "A review of extending performance of epoxy resins using carbon nanomaterials," *Compos. Part B Eng.*, vol. 136, pp. 197–214, 2018, doi: <https://doi.org/10.1016/j.compositesb.2017.08.020>.
- [5] T. Zheng *et al.*, "The curing kinetics and mechanical properties of epoxy resin composites reinforced by PEEK microparticles," *Polym. Test.*, vol. 91, p. 106781, 2020, doi: <https://doi.org/10.1016/j.polymertesting.2020.106781>.
- [6] R. A. Pearson and A. F. Yee, "Toughening mechanisms in elastomer-modified epoxies," *J. Mater. Sci.*, vol. 24, no. 7, pp. 2571–2580, 1989, doi: 10.1007/BF01174528.
- [7] P. Vijayan P., D. Puglia, M. A. S. A. Al-Maadeed, J. M. Kenny, and S. Thomas, "Elastomer/thermoplastic modified epoxy nanocomposites: The hybrid effect of 'micro' and 'nano' scale," *Mater. Sci. Eng. R Reports*, vol. 116, pp. 1–29, 2017, doi: <https://doi.org/10.1016/j.mser.2017.03.001>.
- [8] A. Padinjakkara, *The Role of modified nano fumed silica and nanocellulose in epoxy based polymer blend Submitted in fulfilment of the requirements for the degree of*, no. May. 2020.
- [9] J. Wang, X. Zhang, L. Jiang, and J. Qiao, "Advances in toughened polymer materials by structured rubber particles," *Prog. Polym. Sci.*, vol. 98, p. 101160, 2019, doi: <https://doi.org/10.1016/j.progpolymsci.2019.101160>.
- [10] C. Senthamaraikannan and R. Ramesh, "Evaluation of mechanical and vibration behavior of hybrid epoxy carbon composite beam carrying micron-sized CTBN rubber and nanosilica particles," *Proc. Inst. Mech. Eng. Part L J. Mater. Des. Appl.*, vol. 233, no. 9, pp. 1738–1752, 2019, doi: 10.1177/1464420718784315.
- [11] S. Awang Ngah and A. C. Taylor, "Fracture behaviour of rubber- and silica nanoparticle-toughened glass fibre composites under static and fatigue loading," *Compos. Part A Appl. Sci. Manuf.*, vol. 109, pp. 239–256, 2018, doi: <https://doi.org/10.1016/j.compositesa.2018.02.028>.
- [12] Y. A. Rao, K. Ramji, P. S. Rao, and I. Srikanth, "Effect of A-MWCNTs and ETBN toughener on impact, compression and damping properties of carbon fiber reinforced epoxy composites," *J. Mater. Res. Technol.*, vol. 8, no. 1, pp. 896–903, 2019, doi: <https://doi.org/10.1016/j.jmrt.2018.07.003>.
- [13] N. Chikhi, S. Fellahi, and M. Bakar, "Modification of epoxy resin using reactive liquid (ATBN) rubber," *Eur. Polym. J.*, vol. 38, no. 2, pp. 251–264, 2002, doi: [https://doi.org/10.1016/S0014-3057\(01\)00194-X](https://doi.org/10.1016/S0014-3057(01)00194-X).
- [14] S. Thomas, C. Sinturel, and R. Thomas,

- Micro and Nanostructured Epoxy / Rubber Blends*. Wiley, 2014. [Online]. Available: <https://books.google.co.in/books?id=4Pt wBAAAQBAJ>
- [15] C. M. P and A. C. Dechamma D, "Toughening of unsaturated polyester resin by solid elastomers and liquid rubbers: A review," *Int. Res. J. Eng. Technol.*, no. May, 2021, [Online]. Available: [www.irjet.net](http://www.irjet.net)
- [16] V. C. Chandrasekaran, "1 - Introduction," in *Essential Rubber Formulary*, V. C. Chandrasekaran, Ed., in *Plastics Design Library*, Norwich, NY: William Andrew Publishing, 2007, pp. 3–4. doi: <https://doi.org/10.1016/B978-081551539-5.50002-X>.
- [17] X. Mi *et al.*, "Toughness and its mechanisms in epoxy resins," *Prog. Mater. Sci.*, vol. 130, p. 100977, 2022, doi: <https://doi.org/10.1016/j.pmatsci.2022.100977>.
- [18] Z. Chen and R. Yu, "Study on the synergistic effect of novel phenolic curing agent containing diphenyl ether and OMMT on the cured multifunctional epoxy grafted by CTBN," *Mater. Today Commun.*, vol. 38, p. 108306, 2024, doi: <https://doi.org/10.1016/j.mtcomm.2024.108306>.
- [19] M. Turkben, S. Kocaman, N. Özmeral, U. Soydal, A. Cerit, and G. Ahmetli, "Sustainable production of recycled rubber waste composites with various epoxy systems: A comparative study on mechanical and thermal properties," *Ind. Crops Prod.*, vol. 195, p. 116490, 2023, doi: <https://doi.org/10.1016/j.indcrop.2023.116490>.
- [20] Y. N. Baghdadi *et al.*, "The effects of modified zinc oxide nanoparticles on the mechanical/thermal properties of epoxy resin," *J. Appl. Polym. Sci.*, vol. 137, no. 43, p. 49330, 2020, doi: <https://doi.org/10.1002/app.49330>.
- [21] M. M. El-Masry, R. Ramadan, and M. K. Ahmed, "The effect of adding cobalt ferrite nanoparticles on the mechanical properties of epoxy resin," *Results Mater.*, vol. 8, p. 100160, 2020, doi: <https://doi.org/10.1016/j.rinma.2020.100160>.
- [22] J. K. Kim, P. Saha, S. Thomas, J. T. Haponiuk, and M. K. Aswathi, Eds., *Rubber Recycling: Challenges and Developments*. The Royal Society of Chemistry, 2018. doi: 10.1039/9781788013482.
- [23] F. D. B. de Sousa, "Recycling of Ground Tire Rubber According to the Literature," in *Recycled Polymer Blends and Composites: Processing, Properties, and Applications*, H. Ismail, S. S. M., and I. R. A., Eds., Cham: Springer International Publishing, 2023, pp. 97–110. doi: 10.1007/978-3-031-37046-5\_6.
- [24] A. Rani, S. Tyagi, A. Singh, A. Goel, S. K. Singh, and A. Chauhan, "Sustainable manufacturing for rubber waste industries with integrated circular economy," *Discov. Sustain.*, vol. 6, no. 1, p. 263, 2025, doi: 10.1007/s43621-025-00969-5.
- [25] H. Weia and W. X., Danyong Wangb, "Strengthening and Toughening Technology of Epoxy Resin," *J. Phys. Conf. Ser.*, 2023, doi: 10.1088/1742-6596/2468/1/012066.
- [26] A. Ozturk, C. Kaynak, and T. Tincer, "Effects of liquid rubber modification on the behaviour of epoxy resin," *Eur. Polym. J.*, vol. 37, no. 12, pp. 2353–2363, 2001, doi: [https://doi.org/10.1016/S0014-3057\(01\)00158-6](https://doi.org/10.1016/S0014-3057(01)00158-6).
- [27] S. Grishchuk, L. Sorochnynska, O. C. Vorster, and J. Karger-Kocsis, "Structure, thermal, and mechanical properties of DDM-hardened epoxy/benzoxazine hybrids: Effects of epoxy resin functionality and ETBN toughening," *J. Appl. Polym. Sci.*, vol. 127, no. 6, pp. 5082–5093, 2013, doi: <https://doi.org/10.1002/app.38123>.
- [28] D. Chen *et al.*, "A new strategy to improve the toughness of epoxy thermosets by introducing the thermoplastic epoxy," *Polymer (Guildf.)*, vol. 240, p. 124518, 2022, doi: <https://doi.org/10.1016/j.polymer.2022.124518>.
- [29] and C. Q. Li, Hongfeng, Liwei Zhao, Kai Su, Hao Feng, Dezhi Wang, "A Comparative Study on the Rheological, Thermal, and Mechanical Performance of Epoxy Resin Modified with Thermoplastics," *J. Adhes. Sci. Technol.*, vol. 35, no. 13, pp. 1393–1403, 2020, doi: 10.1080/01694243.2020.1849982.
- [30] P. Xu *et al.*, "Phase structure characterization and compatibilization mechanism of epoxy asphalt modified by thermoplastic elastomer (SBS)," *Constr. Build. Mater.*, vol. 320, p. 126262, 2022, doi: <https://doi.org/10.1016/j.conbuildm.2021.126262>.
- [31] W. Zhou *et al.*, "Advances in Liquid Crystal Epoxy: Molecular Structures, Thermal Conductivity, and Promising Applications in Thermal Management," *ENERGY \& Environ. Mater.*, vol. 7, no. 4, p. e12698, 2024, doi:

- https://doi.org/10.1002/eem2.12698.
- [32] K. Ruan, X. Zhong, X. Shi, J. Dang, and J. Gu, "Liquid crystal epoxy resins with high intrinsic thermal conductivities and their composites: A mini-review," *Mater. Today Phys.*, vol. 20, p. 100456, 2021, doi: https://doi.org/10.1016/j.mtphys.2021.100456.
- [33] Q. Wu, H. Ye, X. Yang, H. Liu, H. Chen, and W. Li, "Synthesis of epoxy resin/silicone rubber interpenetrating polymer network for ablation thermal protection coating," *Polym. Degrad. Stab.*, vol. 215, p. 110454, 2023, doi: https://doi.org/10.1016/j.polymdegradstab.2023.110454.
- [34] B. Pang *et al.*, "The interpenetration polymer network in a cement paste-waterborne epoxy system," *Cem. Concr. Res.*, vol. 139, p. 106236, 2021, doi: https://doi.org/10.1016/j.cemconres.2020.106236.
- [35] Z. Heng *et al.*, "In-situ constructing ultra-high-aspect-ratio core-shell nanostructures to achieve high-performance epoxy thermosets and their carbon fiber reinforced epoxy composites," *Chem. Eng. J.*, vol. 448, p. 137707, 2022, doi: https://doi.org/10.1016/j.cej.2022.137707.
- [36] W. Su *et al.*, "Microstructure and performance of epoxy asphalt binders modified by core-shell rubbers containing different core polymers," *Constr. Build. Mater.*, vol. 304, p. 124689, 2021, doi: https://doi.org/10.1016/j.conbuildmat.2021.124689.
- [37] N. Ning, Y. Qiu, and Y. Wei, "Building effective core/shell polymer nanoparticles for epoxy composite toughening based on Hansen solubility parameters," *Nanotechnol. Rev.*, vol. 10, no. 1, pp. 1183–1196, 2021, doi: doi:10.1515/ntrev-2021-0077.
- [38] S. Yang, R. Li, H. Zhu, Y. Qin, and C. Huang, "Review of the state-of-the-art techniques for enhancing the toughness of thermosetting epoxy asphalt," *Constr. Build. Mater.*, vol. 449, p. 137660, 2024, doi: https://doi.org/10.1016/j.conbuildmat.2024.137660.
- [39] M. Lee *et al.*, "Amphiphilic block copolymer and silica reinforced epoxy composite with excellent toughness and delamination resistance for durable electronic packaging application," *Polymer (Guildf.)*, vol. 245, p. 124679, 2022, doi: https://doi.org/10.1016/j.polymer.2022.124679.
- [40] V. Pang, Z. J. Thompson, G. D. Joly, F. S. Bates, and L. F. Francis, "Adhesion of Silica and Block Copolymer Toughened Epoxy Composites," *ACS Appl. Polym. Mater.*, vol. 4, no. 8, pp. 6169–6178, 2022, doi: 10.1021/acsapm.2c00948.
- [41] J. Long, C. Li, and Y. Li, "Enhancement of Mechanical and Bond Properties of Epoxy Adhesives Modified by SiO<sub>2</sub> Nanoparticles with Active Groups," *Polymers (Basel)*, vol. 14, no. 10, 2022, doi: 10.3390/polym14102052.
- [42] S. R. Mousavi *et al.*, "A review of electrical and thermal conductivities of epoxy resin systems reinforced with carbon nanotubes and graphene-based nanoparticles," *Polym. Test.*, vol. 112, p. 107645, 2022, doi: https://doi.org/10.1016/j.polymertesting.2022.107645.
- [43] A. Mostovoy, A. Shcherbakov, A. Yakovlev, S. Arzamastsev, and M. Lopukhova, "Reinforced Epoxy Composites Modified with Functionalized Graphene Oxide," *Polymers (Basel)*, vol. 14, no. 2, 2022, doi: 10.3390/polym14020338.
- [44] R. Lv, Y. Ren, H. Guo, and S. Bai, "Recent progress on thermal conductivity of graphene filled epoxy composites," *Nano Mater. Sci.*, vol. 4, no. 3, pp. 205–219, 2022, doi: https://doi.org/10.1016/j.nanoms.2021.06.001.
- [45] C. Qiu *et al.*, "Thermal Degradation Behavior and Mechanism of Organosilicon Modified Epoxy Resin," *Macromol. Chem. Phys.*, vol. 223, no. 20, p. 2200164, 2022, doi: https://doi.org/10.1002/macp.202200164.
- [46] Huntsman, "Araldite ® Casting System - Product Info."
- [47] T. Datasheet and P. Description, "Technical Datasheet Carboxyl-Terminated Butadiene-Acrylonitrile," pp. 1–4, 2020.
- [48] E. T. Butadiene-acrylonitrile, V. E. Resins, and I. Applications, "Huntsman Advanced Materials," no. August, pp. 1–3, 2020.
- [49] K. Deshmukh, T. Kovářík, A. Muzaffar, M. Basheer Ahamed, and S. K. Khadheer Pasha, "Chapter 4 - Mechanical analysis of polymers," in *Polymer Science and Innovative Applications*, M. A. A. AlMaadeed, D. Ponnamma, and M. A. Carignano, Eds., Elsevier, 2020, pp. 117–152. doi: https://doi.org/10.1016/B978-0-12-816808-0.00004-4.

- [50] T. T. Hawal, M. S. Patil, R. M. Kulkarni, and S. N. Nandurkar, "Synergetic effect of rubber on the tensile and flexural properties of graphene based epoxy-carbon fiber hybrid nanocomposite," *Mater. Today Proc.*, vol. 27, pp. 515–518, 2020, doi: <https://doi.org/10.1016/j.matpr.2019.11.315>.
- [51] S. Wang *et al.*, "Nano-silica reinforced epoxy resin/nano-rubber composite material with a balance of stiffness and toughness," *High Perform. Polym.*, vol. 33, no. 6, pp. 685–694, 2021, doi: [10.1177/0954008320988752](https://doi.org/10.1177/0954008320988752).
- [52] S. Bao *et al.*, "Synergistic effect of compound rubber and SiO<sub>2</sub> nanoparticles on low-temperature toughening and balanced stiffness-toughness of random copolymer polypropylene nanocomposites," *Compos. Sci. Technol.*, vol. 242, p. 110210, 2023, doi: <https://doi.org/10.1016/j.compscitech.2023.110210>.
- [53] R. da Silva, "Equations for flexural tests: three- and four-point bending," 2022. doi: [10.5281/zenodo.7301896](https://doi.org/10.5281/zenodo.7301896).
- [54] D. F. Beer, Ferdinand P and Johnston Jr, E Russell and DeWolf, John T and Mazurek, *Mechanics of materials*. McGraw Hill, 2006.
- [55] Y. Kim, S. Lee, and H. Yoon, "Fire-Safe Polymer Composites: Flame-Retardant Effect of Nanofillers," *Polymers (Basel)*, vol. 13, no. 4, 2021, doi: [10.3390/polym13040540](https://doi.org/10.3390/polym13040540).
- [56] A. Dasari, Z.-Z. Yu, G.-P. Cai, and Y.-W. Mai, "Recent developments in the fire retardancy of polymeric materials," *Prog. Polym. Sci.*, vol. 38, no. 9, pp. 1357–1387, 2013, doi: <https://doi.org/10.1016/j.progpolymsci.2013.06.006>.
- [57] R. Bagheri, B. T. Marouf, and R. A. Pearson, "Rubber-Toughened Epoxies: A Critical Review," *Polym. Rev.*, vol. 49, no. 3, pp. 201–225, 2009, doi: [10.1080/15583720903048227](https://doi.org/10.1080/15583720903048227).
- [58] A. J. Kinloch, S. J. Shaw, D. A. Tod, and D. L. Hunston, "Deformation and fracture behaviour of a rubber-toughened epoxy: 1. Microstructure and fracture studies," *Polymer (Guildf)*, vol. 24, no. 10, pp. 1341–1354, 1983, doi: [https://doi.org/10.1016/0032-3861\(83\)90070-8](https://doi.org/10.1016/0032-3861(83)90070-8).
- [59] Z. Sun *et al.*, "Enhancing the Mechanical and Thermal Properties of Epoxy Resin via Blending with Thermoplastic Polysulfone," *Polymers (Basel)*, vol. 11, no. 3, 2019, doi: [10.3390/polym11030461](https://doi.org/10.3390/polym11030461).
- [60] M. Bakar, R. Duk, M. Przybytek, and M. Kostrzewa, "Mechanical and Thermal Properties of Epoxy Resin Modified with Polyurethane," *J. Reinf. Plast. Compos.*, vol. 28, no. 17, pp. 2107–2118, 2009, doi: [10.1177/0731684408091703](https://doi.org/10.1177/0731684408091703).
- [61] D. Bazrgari, F. Moztafzadeh, A. A. Sabbagh-Alvani, M. Rasoulianboroujeni, M. Tahriri, and L. Tayebi, "Mechanical properties and tribological performance of epoxy/Al<sub>2</sub>O<sub>3</sub> nanocomposite," *Ceram. Int.*, vol. 44, no. 1, pp. 1220–1224, 2018, doi: <https://doi.org/10.1016/j.ceramint.2017.10.068>.
- [62] B. S. Mustafa, G. M. Jamal, and O. Gh. Abdullah, "Improving the tensile, toughness, and flexural properties of epoxy resin based nanocomposites filled with ZrO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub> nanoparticles," *Results Phys.*, vol. 38, p. 105662, 2022, doi: <https://doi.org/10.1016/j.rinp.2022.105662>.
- [63] A. Banan, A. Ebadirad, and Y. Ebrahimabadi, "Effect of epoxidized liquid CTBN on thermal, mechanical, and rheological properties of epoxy resin," vol. 10, pp. 13–19, 2024, doi: [10.22036/org.chem.2024.455826.1337](https://doi.org/10.22036/org.chem.2024.455826.1337).
- [64] J.-P. Yang, Z.-K. Chen, G. Yang, S.-Y. Fu, and L. Ye, "Simultaneous improvements in the cryogenic tensile strength, ductility and impact strength of epoxy resins by a hyperbranched polymer," *Polymer (Guildf)*, vol. 49, no. 13, pp. 3168–3175, 2008, doi: <https://doi.org/10.1016/j.polymer.2008.05.008>.
- [65] K. A. Denish Davis, Francis Mathew, Jamaludheen. K.P, N. Seenivasaraja, "Design and Analysis of Different Types of Aircraft Radome," *Int. J. Eng. Res. Technol. NCRAIME*, vol. 3, no. 26, 2015, doi: [10.17577/IJERTCONV3IS26038](https://doi.org/10.17577/IJERTCONV3IS26038).