

Article

Halloysite Nanotubes Reinforced Epoxy/Epoxy Acrylate Blends: Unlocking the Potential of Hybrid Nanocomposites

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Abstract

Unlocking the potential of polymer blends requires innovative strategies that transcend simple mixing. This study presents a novel approach by creating hybrid blends of epoxy and structurally compatible in situ synthesized epoxy acrylate (vinyl ester) resins, further reinforced with halloysite nanotubes (HNTs). We went beyond simple blending by synthesizing the epoxy acrylate (EA) component from the base epoxy resin, ensuring molecular-level compatibility. The epoxy acrylate was successfully synthesized via a ring-opening reaction, as confirmed by FTIR and ¹H-NMR. A series of blends at varying weight ratios of epoxy/epoxy acrylate (75/25, 50/50, and 25/75) was prepared and optimized using dynamic mechanical analysis (DMA) for the best viscoelastic performance and subsequently reinforced with 2 wt% HNTs. Our findings reveal that this unique approach fosters highly interpenetrated polymer networks (IPNs), as evidenced by thermal and viscoelastic behavior. The hybrid epoxy nanocomposite with a 75/25 blend ratio exhibits a superior balance of properties, demonstrating a synergistic enhancement in both thermal and thermomechanical properties compared to the neat epoxy and epoxy acrylate networks. The optimized hybrid epoxy composite exhibits a 147% increase in storage modulus (E') and a 180% increase in loss modulus (E'') over the neat epoxy composite while enhancing thermal stability. This study not only presents HNT-reinforced epoxy/epoxy acrylate as a new family of robust hybrid nanocomposites but also provides a fundamental blueprint for compatibilizing and reinforcing thermoset blends for advanced applications.

Keywords: halloysite nanotubes (HNTs); epoxy; epoxy acrylate; composites; interpenetrating polymer network (IPN); dynamic mechanical analysis (DMA); thermal properties; viscoelastic properties

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1. Introduction

Epoxy resins are the cornerstone of high-performance thermosetting polymers, renowned for their exceptional mechanical properties, strong adhesion, chemical resistance, and excellent thermal stability [1,2]. These attributes make them indispensable in a myriad of advanced applications, including aerospace composites, electronic encapsulants, protective coatings, and structural adhesives [3–6]. The cross-linked network structure of epoxies, typically formed through a reaction with various hardeners, is primarily responsible for this robust performance profile. However, this densely cross-linked architecture

also confers a major intrinsic drawback: inherent brittleness and low resistance to crack propagation [7,8].

Extensive research has been dedicated to toughening epoxy resins without critically compromising their desirable thermal and mechanical properties. Early strategies involved the incorporation of liquid rubbers, such as carboxyl-terminated butadiene acrylonitrile (CTBN), which precipitate upon curing to form a dispersed phase of rubbery particles that induce energy-dissipation mechanisms [9]. While effective in enhancing toughness, this approach often leads to a substantial reduction in modulus, strength, and glass transition temperature (T_g) [10]. Alternative methodologies have explored blending epoxies with thermoplastics (e.g., poly(ether sulfone) and poly(ether imide)), which can improve toughness but often introduce processing complexities and may not provide a sufficient balance of properties [11]. Consequently, the pursuit of a method that simultaneously enhances toughness and maintains or even improves stiffness and thermal properties remains a significant challenge.

A particularly promising avenue is the formation of hybrid thermoset systems or interpenetrating polymer networks (IPNs) [12]. Interpenetrating polymer networks (IPNs) represent a sophisticated class of polymer blends designed to achieve synergistic property combinations that are unattainable from their individual components. By definition, an IPN is a material comprising two or more polymer networks that are synthesized and/or cross-linked in the presence of one another, creating a unique “network-within-network” structure that physically entraps the constituent polymers and suppresses macroscopic phase separation [12,13]. This architecture facilitates a finer level of mixing compared to simple blends or composites, often leading to superior mechanical performance, enhanced damping characteristics, and better dimensional stability [14]. The concept of IPNs provides a powerful toolbox for tailoring material properties; for instance, combining a rigid, high-modulus polymer (like an epoxy) with a ductile, energy-absorbing polymer (like an epoxy acrylate) can yield a hybrid system that overcomes the classic toughness–strength trade-off [15]. The versatility of the IPN strategy is demonstrated by its application across a wide range of polymer pairs, e.g., polyurethane/acrylate, polyacrylamide/polyacrylic acid, silicon/polyurethane, unsaturated polyester/poly(vinyl acetate), vinyl ester/polyetherimide, bismaleimide/polyetherimide, polybenzoxazine/polyurethane, bismaleimide/polyurethane, cyanate ester/polysulfone, cyanate ester/polyurethane, vinyl ester/cyanate ester, etc.

IPNs formed from diglycidyl ether of bisphenol A (DGEBA) epoxy and a polyurethane (PU) prepolymer have been shown to achieve a remarkable synergy, significantly enhancing impact strength and fracture toughness while maintaining a high modulus and thermal stability, with the morphology and final properties being tunable by the PU/epoxy ratio [16–22]. Similarly, epoxy/acrylate IPNs have been extensively investigated. Systems incorporating epoxy with methyl methacrylate (MMA) or other acrylates result in transparent materials exhibiting a fine co-continuous morphology, which leads to a substantial improvement in tensile strength, hardness, and damping characteristics compared to the neat epoxy resin [23–28]. Another significant blend is between epoxy and cyanate ester, which forms a highly cross-linked network known as a simultaneous interpenetrating network (SIN). These high-performance IPNs exhibit an elevated glass transition temperature (T_g), often exceeding that of the individual polymers, alongside superior thermal stability and low moisture absorption, making them ideal for advanced aerospace applications [29,30]. Numerous other epoxy-based IPNs have been investigated, including those with novolac [31], polydicyclopentadiene [32], silicon rubber [33], bismaleimide–triazine [34], polyimide [35,36], epoxidized soybean oil [37,38], polydimethylsiloxane [39,40], polydicyclopentadiene [41], etc. These studies collectively affirm that creating an IPN architecture with epoxy is a versatile method to circumvent the brittleness

of epoxy without forfeiting its inherent advantages, enabling the tailoring of final properties through the careful selection of the second polymer component. The properties of the resulting IPN are highly dependent on the degree of interpenetration, cross-link density, and the compatibility between the two networks, which can be engineered through careful selection of monomers, cross-linkers, and curing protocols [42].

In the context of IPNs, the combination of epoxy resins with epoxy acrylates (also known as vinyl esters) has garnered interest. Epoxy acrylates, synthesized by the esterification of an epoxy resin with unsaturated acids like acrylic acid, possess a backbone similar to the parent epoxy, promoting compatibility, and terminal vinyl groups that enable free-radical polymerization. This unique chemistry allows for the creation of dual-cure systems, where epoxy curing (e.g., via an anhydride) and acrylate polymerization (e.g., via a thermal initiator) can occur concurrently, potentially leading to a synergistic, interpenetrating network architecture. Such IPN-like structures are hypothesized to facilitate a more effective dissipation of mechanical energy, thereby overcoming the traditional toughness–strength trade-off.

Parallel to the development of polymer blends, nanoscale reinforcement has emerged as a powerful tool for tailoring material properties. Among various nanofillers, halloysite nanotubes (HNTs) have recently attracted considerable attention due to their unique combination of characteristics [43]. HNTs are naturally occurring aluminosilicate clays (empirical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_2$) with a distinctive hollow tubular structure, high aspect ratio, and low hydroxyl group density on their outer surface, which promotes better dispersion in polymer matrices compared to other clays like montmorillonite [44,45]. HNTs form as a result of the hydrothermal alteration of clay minerals derived from aluminum silicates [46]. A key advantage of halloysite nanotubes (HNTs) is their high aspect ratio and tubular morphology, which are similar to carbon nanotubes (CNTs). However, unlike CNTs, HNTs are naturally occurring, abundantly available, cost-effective, environmentally friendly, and offer superior processing compatibility. Their potential as nano-reinforcements to enhance mechanical strength, thermal stability, and flame retardancy in epoxy systems has been well-documented [8,44,47,48]. Critically, HNTs can also act as nanoscale toughening agents by mechanisms such as crack bridging and nanotube pull-out [49]. Unlike many high-aspect-ratio nanofillers, e.g., CNTs, which severely scatter light and render polymer composites opaque, HNTs largely preserve the optical clarity of the matrix at moderate wt% loadings, offering a distinct advantage for applications where transparency is desirable.

Herein, we report on the design, fabrication, and comprehensive characterization of a novel series of hybrid nanocomposites based on DGEBA epoxy and a custom-synthesized epoxy acrylate, reinforced with halloysite nanotubes. The epoxy acrylate was synthesized in situ from the base DGEBA resin to ensure maximum molecular compatibility. Such an epoxy modifier is expected to facilitate the miscibility and interphase continuity when blended with the parent epoxy. The blends were fabricated and optimized at varying mass ratios for their dynamic mechanical performance and subsequently reinforced with an optimized loading of 2 wt% HNTs. The utilization of halloysite nanotubes in the current work is expected not only to provide classical nano-reinforcement but also to potentially compatibilize the two networks and act as centers for stress transfer, leading to a material whose properties are greater than the sum of its parts. Advantageously, this approach utilizes commodity materials, combined with the use of inexpensive and environmentally benign halloysite nanotubes, employing a simple, solvent-free, facile mixing process. This study systematically investigates the chemical, morphological, thermal, and mechanical properties of these hybrid systems. We demonstrate that the specific architecture of the HNT-reinforced epoxy/epoxy acrylate blend leads to a highly compatible, interpenetrated network, resulting in a superior and tunable balance of strength and toughness,

thereby unlocking a new pathway for designing advanced polymer composites. The reported approach provides a highly practical and industrially viable pathway to advanced materials for demanding engineering applications.

2. Materials and Methods

2.1. Materials

The halloysite nanotubes (empirical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_2$) were purchased by NaturalNano Inc. (Rochester, NY, USA). The HNTs had a tube length that varied between 500 nm and 1.2 μm , a diameter of <100 nm, and a surface area of 48.58 m^2/g , as determined by Brunauer–Emmett–Teller (BET). Acrylic acid (anhydrous, 99%) and potassium persulfate (ACS reagent, $\geq 99.0\%$) were purchased from Sigma Aldrich (St. Louis, MO, USA). “Araldite F” epoxy resin of diglycidyl ether of bisphenol A (DGEBA) with an epoxy content of $\sim 5.25 \text{ Eq/kg}$, “Araldite HY 905” hardener (methyltetrahydrophthalic anhydride), and “Accelerator DY 061” catalytic accelerator (2,4,6-tris(dimethylaminomethyl)phenol) were purchased from Huntsman Corporation (The Woodlands, TX, USA). All chemicals were used as received without any additional purification.

2.2. Preparation of Epoxy Acrylate from Epoxy Resin

The epoxy acrylate (vinyl ester) resin was synthesized via a ring-opening acrylation reaction. A stoichiometric mixture of Araldite F and acrylic acid, in a 2:1 molar ratio of epoxy groups to carboxylic acid groups, was prepared in a Schlenk flask. To prevent premature free-radical polymerization, the reaction was assembled under an inert nitrogen atmosphere within a glove box. 2,4,6-tris(dimethylaminomethyl)phenol was employed as a catalyst at a loading of 1 wt% relative to the total reaction mass. The mixture was then heated to 70 $^\circ\text{C}$ with constant magnetic stirring on a hot plate for a duration of 4 h to facilitate the reaction, as outlined in Figure 1. The completion of the acrylation reaction was monitored by collecting samples from the reaction mixture and analyzing them using proton nuclear magnetic resonance (^1H NMR) and Fourier-transform infrared (FTIR).

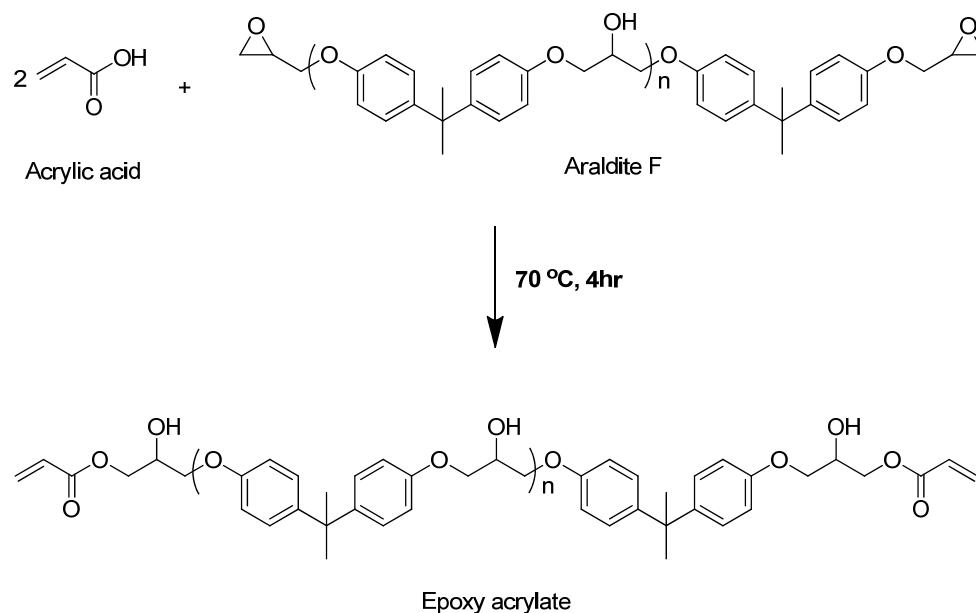


Figure 1. Chemical route to prepare epoxy acrylate.

2.3. Preparation of Epoxy/Epoxy Acrylate Blends and Their HNT Nanocomposites

The epoxy/epoxy acrylate blends were prepared by blending the prepared epoxy acrylate resin (vinyl ester) with the epoxy resin/hardener mixture at varying wt% loading ratios (i.e., epoxy: epoxy acrylate; 75:25, 50:50, 25:75), as shown in Table 1. Predetermined amounts of Araldite F (DGEBA, epoxy resin), a stoichiometric amount of Araldite HY 905 (hardener), and synthesized epoxy acrylate were taken in a beaker to form blends. The mixture was mechanically mixed using a mechanical stirrer. The DY 061 (accelerator, 0.5 wt%) and potassium persulfate (initiator, 0.5 wt%) were added to the mixture just before the end of stirring to catalyze the epoxy–anhydride and epoxy acrylate polymerization reactions, respectively, and the mixture was immediately poured into silicon molds and degassed in a vacuum oven to remove entrapped air for subsequent thermal curing. The neat epoxy (as a control) was cured in a similar way using Araldite F (epoxy resin) and a stoichiometric amount of Araldite HY 905 (hardener). Accelerator DY 061 (a tertiary amine) catalyzed the epoxy–anhydride step-growth polymerization, while potassium persulfate (KPS) thermally decomposed to generate free radicals, initiating the chain-growth polymerization of the epoxy acrylate vinyl groups. The simultaneous presence of DY 061 and KPS enabled controlled and concurrent development of the epoxy and acrylate networks, favoring the formation of a chemically compatible and well-integrated interpenetrating polymer network.

Table 1. Sample code designations.

Sample Code	Assignment Details
E	Epoxy resin
EA	Epoxy acrylate
<i>Cured epoxy/epoxy acrylate blends EEA-(wt%:wt%)</i>	
EEA-(75/25)	epoxy/epoxy acrylate blends (75 wt%:25 wt%)
EEA-(50/50)	epoxy/epoxy acrylate blends (50 wt%:50 wt%)
EEA-(25/75)	epoxy/epoxy acrylate blends (25 wt%:75 wt%)

The optimized composition of the epoxy/epoxy acrylate blend was also reinforced with halloysite nanotubes (HNTs) at 2 wt% loading, an optimized amount previously determined from our prior studies, which yielded an optimal balance of dispersion and mechanical enhancement without aggregation on the base epoxy system [49]. For this, first, Araldite F epoxy resin and synthesized epoxy acrylate were taken in a beaker along with HNTs. To achieve a homogeneous dispersion of the HNTs, the resin mixture was first subjected to mechanical stirring at a low speed, followed by ultrasonication in a bath sonicator for 30 min. A stoichiometric quantity of Araldite HY 905 anhydride hardener was then incorporated into the mixture under mechanical stirring. Immediately prior to the completion of mixing, Accelerator DY 061 (0.5 wt%) and potassium persulfate (KPS, 0.5 wt%) were added. The final mixture was promptly transferred to a silicone mold and degassed. The curing protocol consisted of a primary step at 100 °C for 3 h, followed by a post-curing cycle at 120 °C for 1 h to ensure complete thermal cure. The curing protocol was performed using isothermal stages in preset ovens.

2.4. Characterization

2.4.1. ¹H NMR and FTIR Analysis

The successful synthesis of the epoxy acrylate (vinyl ester) was verified using proton nuclear magnetic resonance (¹H NMR) spectroscopy at room temperature. The analysis was performed on a 500 MHz Agilent DirectDrive2 NMR spectrometer (Agilent

Technologies, Palo Alto, CA, USA). For this purpose, approximately 10 mg of the sample was dissolved in 1 mL of deuterated chloroform (CDCl_3) to prepare the solution for analysis.

Furthermore, the synthesis of epoxy acrylate was also confirmed by Fourier-transform infrared (FTIR) spectroscopy. FTIR analysis was performed on a Perkin Elmer Spectrum 100 spectrophotometer (Beaconsfield, UK). The spectra were acquired at room temperature in transmittance mode using an attenuated total reflectance (ATR) accessory. Data collection was carried out over a wavenumber range of 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1} , accumulating 64 scans per spectrum to ensure a high signal-to-noise ratio. The progression of the curing reactions and the accompanying chemical transformations were further monitored using FTIR spectroscopy. The extent of the epoxy–anhydride cure was confirmed by the disappearance of the characteristic oxirane ring absorption band, which indicates the consumption of epoxy groups. Similarly, the free-radical curing of the epoxy acrylate segments was verified by the attenuation of the vinyl ($\text{C}=\text{C}$) stretching vibrations, signifying the polymerization of the acrylate functional groups.

2.4.2. X-Ray Diffraction (XRD)

The crystal structure of pristine halloysite nanotubes (HNTs) was analyzed by X-ray diffraction (XRD) using a Panalytical X'Pert Pro diffractometer (Malvern Panalytical B.V., Almelo, The Netherlands) equipped with a $\text{Cu K}\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$). Measurements were conducted at room temperature in a 2θ range from 10° to 70° , employing a step-scan mode with a step size of 0.01° and a dwell time of 0.5 s per step. The interplanar spacing (d-spacing) was calculated from the diffraction patterns using Bragg's law:

$$d = n\lambda/2\sin\theta \quad (1)$$

where n is the order of reflection, λ is the X-ray wavelength, and θ is the Bragg angle.

2.4.3. Thermal Analysis (TGA, DSC)

The thermal stability and degradation behavior of the samples were evaluated using simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a TA Instruments Q600 thermal analyzer. Samples weighing approximately 5–10 mg were heated in open alumina crucibles from 50°C to 700°C at a constant heating rate of $10^\circ\text{C}/\text{min}$. All experiments were conducted under a continuous nitrogen purge with a flow rate of 100 mL/min to maintain an inert atmosphere and efficiently remove decomposition byproducts. The TGA data provided the residual mass profile (weight loss) as a function of temperature, while the derivative thermogravimetric (DTG) curves were derived from this data to precisely identify the temperatures of maximum degradation rates for individual decomposition steps. Concurrently, the DSC signal was monitored to record thermal transitions, such as glass transitions and exothermic/endothermic events.

2.4.4. Dynamic Mechanical Analysis (DMA)

The viscoelastic behavior of the cured blends and nanocomposites was characterized using dynamic mechanical analysis (DMA) on a TA Instruments Q800 analyzer (V21.1 Build 51). Rectangular specimens of specific dimensions were tested in a cantilever bending mode. The temperature-dependent viscoelastic properties were measured from 50°C to 150°C at a constant heating rate of $2^\circ\text{C}/\text{min}$. The tests were performed at multiple oscillation frequencies (1, 25, and 50 Hz) with a fixed displacement amplitude of $15 \mu\text{m}$ to determine the storage modulus (E'), loss modulus (E''), and loss factor ($\tan \delta$) as functions of temperature.

2.4.5. Scanning Electron Microscopy (SEM)

The morphological features and fracture surfaces of the cured nanocomposites were examined using scanning electron microscopy (SEM) to assess the dispersion state of the halloysite nanotubes (HNTs) and to investigate the failure mechanisms and reinforcing effects under mechanical stress. The analysis was performed employing a JEOL 7500F (JEOL Ltd., Tokyo, Japan) field-emission scanning electron microscope (FE-SEM) at 5.0 kV under high vacuum. To ensure electrical conductivity and prevent charging, the samples were mounted on aluminum stubs and sputter-coated with a thin layer of iridium prior to imaging, as the iridium is an excellent choice for high-resolution imaging because it forms much finer films than gold and is also used for its non-oxidizing properties.

2.4.6. Energy-Dispersive X-Ray Spectroscopy (EDS)

Energy-dispersive X-ray spectroscopy (EDS) was employed to investigate the interfacial interactions and wetting behavior between the halloysite nanotubes (HNTs) and the epoxy matrix by comparing the elemental composition of pristine HNTs with that of the HNTs embedded within the cured composite. The analysis was conducted using a JEOL 7500F FE-SEM equipped with an Oxford Instruments X-Max silicon drift detector (SDD), with data acquisition and processing managed by the Oxford Instruments AZtec software suite (version 3.0, Oxford Instruments, High Wycombe, UK).

The sample code designations and their respective assignment details of epoxy nanocomposites loaded with HNTs are illustrated in Table 1.

3. Results and Discussion

3.1. Proton Nuclear Magnetic Resonance (^1H NMR)

The successful synthesis of the epoxy acrylate (vinyl ester) was confirmed through a comprehensive analysis of the ^1H NMR spectra for the precursors and the final product, as shown in Figure 2a–d. The spectrum of acrylic acid exhibited the characteristic vinyl proton resonances observed at 6.44, 6.16, and 5.87 ppm [50] and a broad signal at 12.06 ppm for the carboxylic acid proton ($-\text{COOH}$). On the other hand, the spectrum of the pristine epoxy resin displayed a definitive peak at approximately 2.62 ppm, corresponding to the methylene protons of the epoxide ring.

Critically, the ^1H NMR spectrum of the synthesized epoxy acrylate (Figure 2a–c) reveals the complete consumption of the starting materials. The disappearance of the epoxide methylene peak at 2.62 ppm and the carboxylic acid proton at 12.06 ppm provides direct evidence of the ring-opening esterification reaction. Concurrently, the appearance of new signals in the region of 4.4–4.5 ppm, attributable to the methylene protons ($-\text{CH}_2-$) adjacent to the newly formed ester group, confirms the formation of the vinyl ester linkage. The persistence of the vinyl proton resonances (5.87, 6.16, 6.44 ppm) in the final product (Figure 2a,d) verifies that the acrylate functionality remains intact, providing the reactive sites for subsequent free-radical curing. The collective NMR evidence conclusively demonstrates the successful synthesis of the target epoxy acrylate oligomer from the disappearance of reactant signatures and the emergence of product-specific peaks.

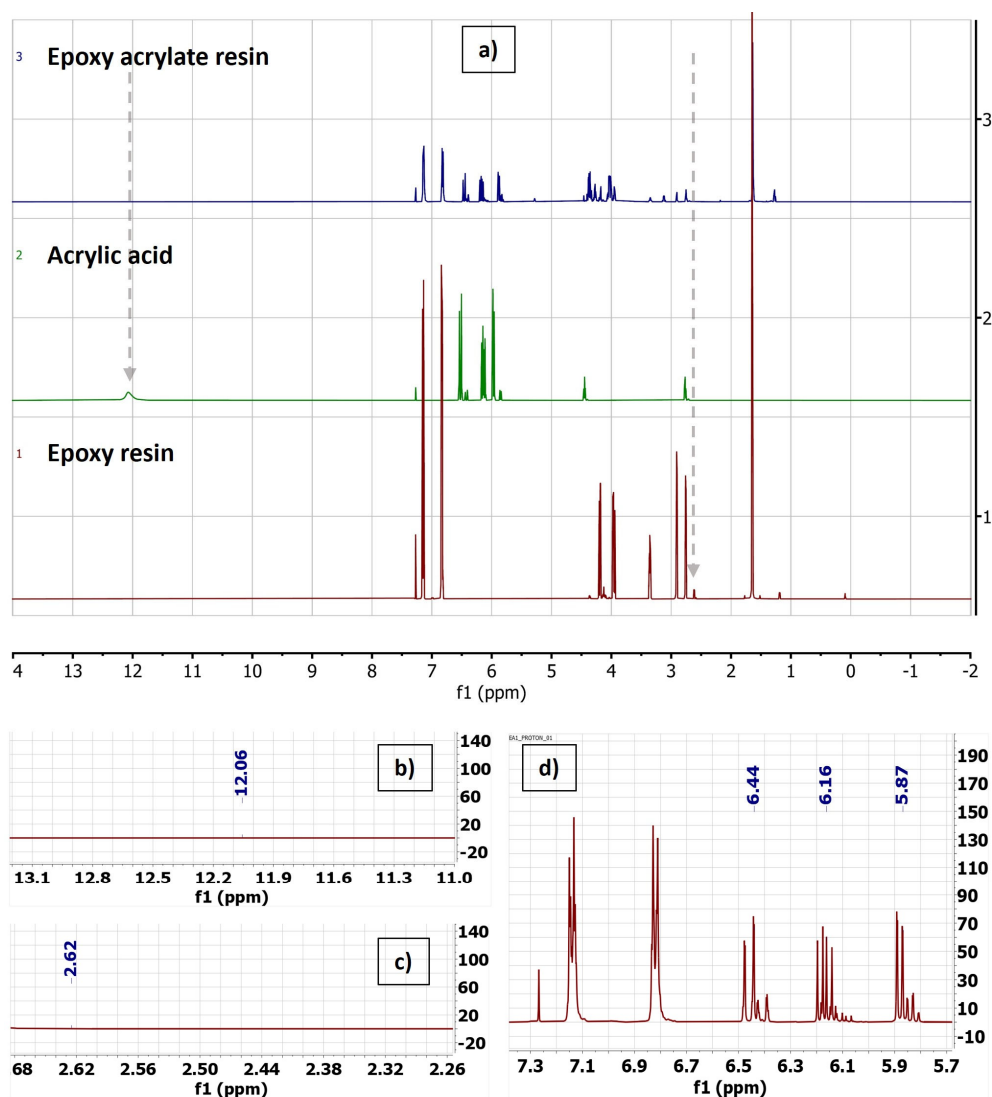


Figure 2. Proton nuclear magnetic resonance (^1H NMR) spectra of (a) prepared epoxy acrylate. The absence of (b) a peak for the hydroxyl group at 12.06 ppm and (c) a methylene group at 2.62 ppm reveals the successful conversion of precursors in epoxy acrylate resin. (d) The appearance of characteristic peaks for the acrylate group of epoxy acrylate is observed at 6.44, 6.16, and 5.87 ppm.

3.2. Fourier-Transform Infrared (FTIR)

The chemical structure of the synthesized epoxy acrylate was further verified by Fourier-transform infrared (FTIR) spectroscopy, with the results corroborating the ^1H NMR analysis (Figure 3a). The FTIR spectrum of the pristine epoxy resin confirmed the presence of the oxirane functional group, indicated by its characteristic absorption band at 910 cm^{-1} [49]. Following the acrylation reaction, the complete disappearance of this band in the epoxy acrylate spectrum confirms the consumption of the epoxy rings. This is consistent with their reaction with the carboxylic acid groups of acrylic acid to form an ester linkage. Furthermore, the appearance of a broad absorption band in the region of 3500 cm^{-1} for the epoxy acrylate is attributed to the stretching vibrations of the secondary hydroxyl groups (-OH) generated from the ring-opening of the epoxide, providing additional evidence of the successful synthesis.

The curing behavior of the epoxy/epoxy acrylate blends was also monitored using FTIR spectroscopy (Figure 3b). The spectrum of the fully cured nanocomposite shows the

absence of the characteristic epoxy ring absorption at 910 cm^{-1} , confirming the completion of the epoxy–anhydride reaction. Simultaneously, the disappearance of the distinct vinyl ($\text{C}=\text{C}$) stretching vibrations from the acrylate functional groups between 1630 and 1650 cm^{-1} indicates the successful free-radical polymerization of the epoxy acrylate segments. The concurrent disappearance of these key reactive peaks provides definitive spectroscopic evidence for the dual-cure mechanism and the successful formation of a cross-linked network within the cured blend.

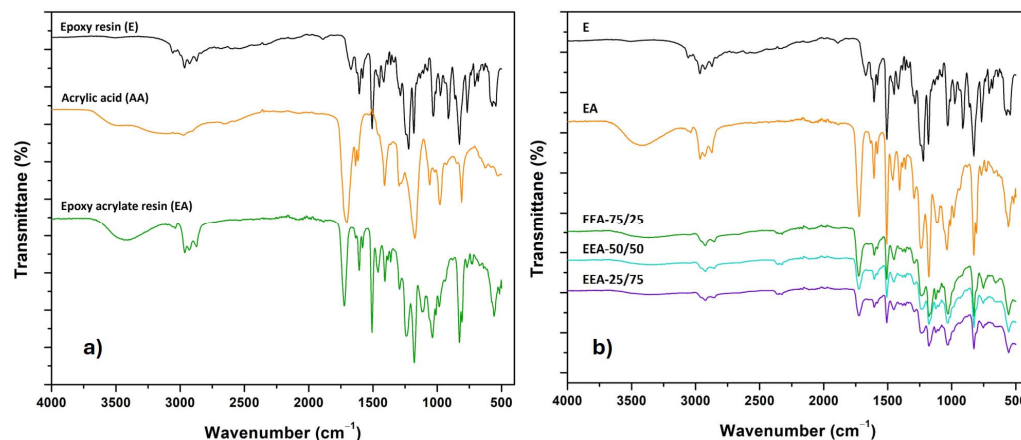


Figure 3. FTIR Spectrum of prepared (a) epoxy acrylate and (b) cured epoxy/epoxy acrylate blends.

3.3. HNTs Characterization

The FTIR spectrum of pristine halloysite nanotubes (HNTs), presented in Figure 4a, exhibits characteristic absorption bands that confirm their aluminosilicate structure. Two sharp bands observed at 3692 cm^{-1} and 3624 cm^{-1} are attributed to the O–H stretching vibrations of the inner-surface and inner hydroxyl groups, respectively, located between the silica and alumina sheets. The intense, broad absorption complex in the region of 1000 – 1100 cm^{-1} , with peaks at 1028 and 1009 cm^{-1} , corresponds to the asymmetric stretching of Si–O–Si bonds. A distinct shoulder at approximately 1118 cm^{-1} is assigned to the stretching vibrations of the apical Si–O bonds. Furthermore, the deformation vibration of the Al–O–H group is evident at 910 cm^{-1} . The spectrum also confirms the halloysite structure with the presence of two lower-frequency bands at 796 and 755 cm^{-1} , which are characteristic of O–H translational modes. These collective features are consistent with the established vibrational fingerprint of halloysite [8,49,51].

The X-ray diffraction (XRD) pattern of pristine halloysite nanotubes (HNTs) is presented in Figure 4b, confirming their characteristic crystal structure. The diffraction profile aligns with the standard for halloysite-7 Å (JCPDS Card 29-1487). A dominant peak is observed at $2\theta = 12.10^\circ$, corresponding to a basal (d_{100}) spacing of 7.30 Å . This reflection originates from the interlayer spacing between the aluminosilicate sheets and is a definitive identifier for the dehydrated 7 Å form (meta-halloysite). A second prominent peak at $2\theta = 20.10^\circ$ (d -spacing = 4.41 Å) is associated with the (002) plane and is a key indicator of the nanotube’s rolled, tubular morphology, distinguishing it from the platy structure of kaolinite. The pattern further confirms the crystalline nature of the HNTs with several distinct reflections at 2θ values of 24.81° (d_{110}), 35.24° , 38.53° , 55.47° , and 62.52° , which correspond to d -spacings of 3.58 , 2.53 , 2.33 , 1.65 , and 1.48 Å , respectively. The presence and positions of all these peaks are consistent with the known crystallographic structure of halloysite [8,49,52].

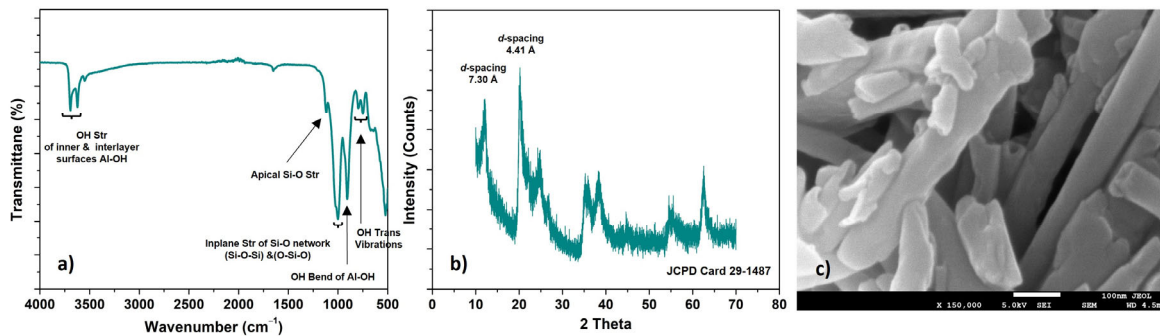


Figure 4. Analysis of pristine halloysite nanotubes (HNTs) by (a) FTIR spectrum, (b) XRD, and (c) SEM.

Figure 4c shows the morphology of the pristine halloysite nanotubes (HNTs). The micrographs confirm the characteristic tubular geometry of the material, with numerous nanotubes displaying a distinct cylindrical form and visible hollow lumens, with an outer diameter distribution ranging from ~40 to 90 nm. The surfaces of the individual nanotubes are smooth, and the particles are largely non-aggregated, exhibiting a random orientation. While halloysite shares a similar aluminosilicate layered structure with kaolinite, its propensity to roll into these well-defined nanotubes constitutes its primary morphological distinction, which is clearly evidenced in the obtained micrographs [53].

3.4. Dynamic Mechanical Analysis (DMA)

The mechanical performance of the prepared epoxy/epoxy acrylate blends, formulated at mass ratios of 75:25, 50:50, and 25:75, was evaluated to identify the optimal composition. The stress–strain behavior of these blends, determined via dynamic mechanical analysis (DMA) at a temperature of 50 °C, is presented in Figure 5a–c. Analysis of these curves reveals a distinct composition–property relationship. The blend containing 25 wt% epoxy acrylate (EEA-75/25) in the epoxy matrix exhibited a superior balance of properties, achieving the highest ultimate strength among all tested formulations. This suggests that a moderate incorporation of the epoxy acrylate phase effectively reinforces the epoxy network, likely through the formation of an interpenetrating network (IPN) structure that enhances stress dissipation and load-bearing capacity without introducing excessive flexibility that could compromise strength. Based on this optimal performance, the EEA-75/25 composition was selected for further investigation. Subsequently, the influence of varying oscillation frequencies (1, 25, and 50 Hz) on the viscoelastic modulus of the EEA-75/25 blend at a temperature of 50 °C was explored to understand its time-dependent mechanical response, as detailed in Figure 5d.

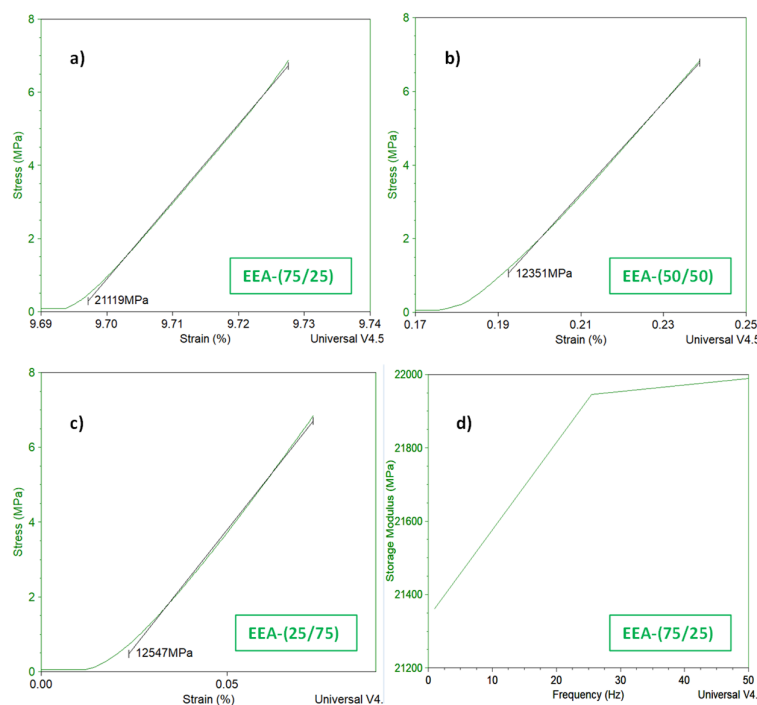


Figure 5. Dynamic mechanical analysis: (a–c) stress–strain curves, (d) storage modulus as a function of frequency for epoxy/epoxy acrylate blends.

The optimized epoxy/epoxy acrylate blend (EEA-75/25) was then subsequently reinforced with 2 wt% halloysite nanotubes (HNTs). The viscoelastic properties of this material were thoroughly investigated using dynamic mechanical analysis (DMA) under a temperature sweep, with key parameters including the storage modulus (E'), loss modulus (E''), damping factor ($\tan \delta$), and Cole–Cole plot presented in Figure 6. DMA is a powerful technique for elucidating the thermomechanical characteristics and microscopic relaxation processes of polymer nanocomposites, providing critical insights for their application in temperature-dependent environments.

3.4.1. Storage Modulus (E')

The storage modulus (E'), which represents the elastic, energy-storing component of the material and is a direct indicator of its stiffness, is plotted as a function of temperature in Figure 6a. The HNT-reinforced nanocomposite exhibited a characteristic viscoelastic response: a high, constant E' in the glassy plateau, followed by a sharp decrease in the temperature range of 70–95 °C, culminating in a low-modulus rubbery plateau. This abrupt decline signifies the glass-to-rubber transition, where cooperative segmental motion of the polymer chains is activated [49]. The high modulus in the glassy state (13,135 MPa at 50 °C) is a consequence of restricted chain mobility within a tightly packed, frozen network, resulting in superior mechanical strength. The storage modulus in the glassy state serves as a direct indicator of a material's strength, with a higher value signifying superior mechanical performance and load-bearing capacity. The transition region, with a step transition (T_{onset}) of 85.55 °C and an endpoint (T_{endset}) of 100.90 °C, resulting in a total transition width of 15.35 °C, marks the progressive breakdown of intermolecular forces and increased chain mobility, leading to the observed softening and modulus loss. The transition from the glassy to the rubbery state occurred with a slope of $-672 \text{ MPa/}^\circ\text{C}$. The preservation of a distinct rubbery plateau confirms the integrity of the cross-linked network even above its glass transition.

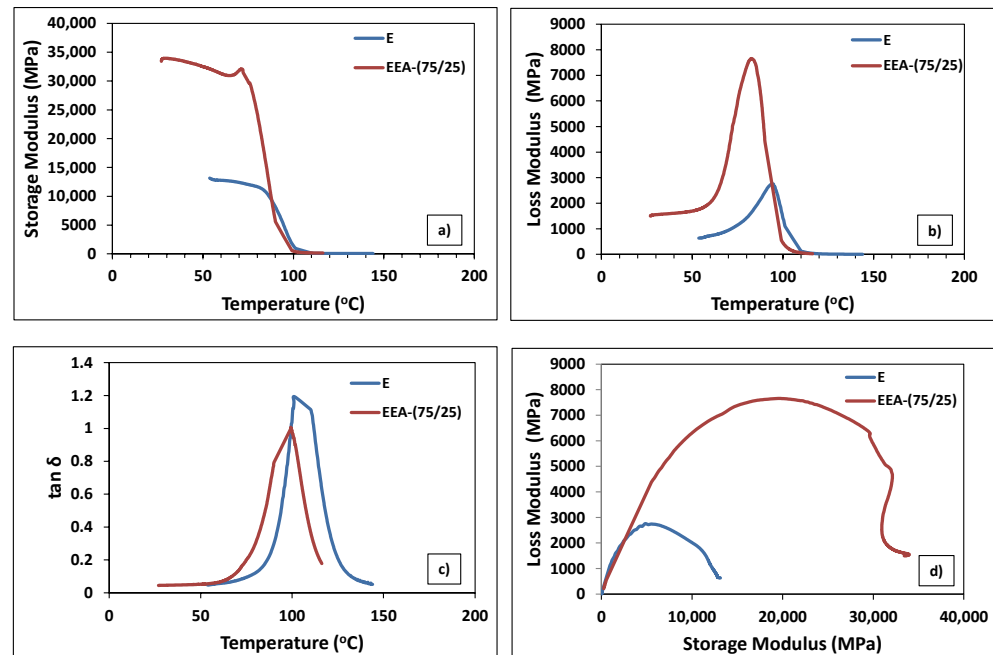


Figure 6. Dynamic mechanical analysis: (a) storage modulus, (b) loss modulus, and (c) $\tan \delta$ as a function of temperature; (d) Cole–Cole plot for epoxy/epoxy acrylate nanocomposites.

In contrast, the reinforced epoxy/epoxy acrylate blend demonstrated a highly distinctive and technologically advantageous behavior. A direct comparison of the glassy state properties immediately highlights the efficacy of the blending strategy. The reinforced epoxy/epoxy acrylate blend showed dramatically higher strength, with an E' of 32,433 MPa at 50 °C. This represents an increase of approximately 147% as compared to unblended reinforced epoxy, unequivocally demonstrating that the incorporation of the epoxy acrylate phase, combined with HNTs, creates a far more rigid network structure in the glassy state. This significant enhancement is likely due to the formation of a denser, interpenetrating network (IPN) that more effectively restricts the segmental motion of polymer chains, supplemented by the reinforcing effect of the nanotubes.

Beyond the glassy state, the materials exhibited fundamentally different transition behaviors. Contrary to the monotonic decline, a significant synergistic increase in E' was observed in the vicinity of the glass transition. Specifically, the storage modulus exhibited an anomalous rise from 30,948 MPa at 64 °C to 32,110 MPa at 71 °C before the onset of the primary drop. This pre-transition stiffening is a non-trivial finding and indicates a complex, cooperative interaction between the epoxy and epoxy acrylate networks. As both epoxy and epoxy acrylate networks are molecularly interpenetrated, not phase separated, this creates a broader spectrum of segmental constraints and regions with different relaxation activation energies. As the temperature approaches T_g , localized mobility increases in the more flexible epoxy acrylate segments, and this mobility allows enhanced stress transfer to HNTs and progressive engagement of the HNT–matrix interphase, as the previously “latent” filler–matrix contacts become mechanically active. Furthermore, the EEA blend underwent a rapid transition to the rubbery state, resulting in a total transition width of 16.47 °C, characterized by a dramatically steeper slope of $-1842 \text{ MPa}/^\circ\text{C}$ compared to the unblended epoxy. This sharp decline is indicative of a more homogeneous network with a narrower distribution of relaxation times. The analysis of the derivative storage modulus (dE'/dT) provides a more sensitive and quantitative measure of the glass transition dynamics, further elucidating the profound differences in the reinforced epoxy/epoxy acrylate blend. The parameters derived from these curves are peak drop

temperature, slope, and integrated area. The reinforced epoxy exhibited a single, broad negative peak in its derivative curve, with a maximum rate of modulus loss ($-43.28 \text{ MPa/}^\circ\text{C}$), and the integrated area under the curve was calculated to be $2144 \text{ MPa}\cdot\text{min/}^\circ\text{C}$. In contrast, the derivative curve for the reinforced EEA blend confirmed the synergistic behavior observed in the primary E' data. The blend displayed a much sharper and more intense transition, with a vastly steeper slope of $-141.8 \text{ MPa/}^\circ\text{C}$ ($\sim 3\times$), indicating a highly cooperative relaxation process. Once the thermal energy is sufficient to overcome the restrictive forces of the integrated network, the transition from a rigid to a soft state occurs in a much more abrupt and concerted manner. This is a hallmark of a more homogeneous and well-defined network architecture. Furthermore, the integrated area under the derivative curve for the EEA blend was $12,932 \text{ MPa}\cdot\text{min/}^\circ\text{C}$, and the value is approximately $\sim 6\times$ larger than that of the control reinforced epoxy. This area is a direct measure of the total energy dissipated during the glass transition. The substantially larger area for the blend signifies a much greater overall change in the material's stiffness. This is consistent with our previous observation of its higher initial glassy modulus; the blend has a greater amount of "rigidity" to lose during the transition, and it does so through a more intense and coordinated molecular relaxation process.

3.4.2. Loss Modulus (E'')

The loss modulus (E''), which quantifies the viscous response and energy dissipated as heat during cyclic deformation, is presented in Figure 6b. The curves for both the reinforced epoxy and the epoxy/epoxy acrylate (EEA) blend exhibit a characteristic peak at the glass transition, corresponding to the temperature of maximum molecular mobility and energy loss [49]. Crucially, the peak loss modulus of the EEA blend is significantly higher than that of the unblended epoxy. This pronounced increase is a direct consequence of the more complex morphology of the hybrid system. The internal friction generated by the restricted motion between the interpenetrating epoxy and epoxy acrylate networks, coupled with the reinforcing interface of the halloysite nanotubes, necessitates greater energy dissipation, thereby resulting in a substantially enhanced viscous response.

The reinforced epoxy/epoxy acrylate (EEA) blend exhibited a peak loss modulus of 7655 MPa , which is 2.8 times greater than that of the reinforced neat epoxy (2738 MPa). This substantial increase indicates a significantly higher capacity for energy dissipation within the EEA blend during deformation. The transition kinetics were also markedly different. The slope to the E'' peak for the EEA blend was $294.3 \text{ MPa/}^\circ\text{C}$, over three times steeper than that of the neat epoxy ($89.17 \text{ MPa/}^\circ\text{C}$). This demonstrates a more rapid and cooperative mobilization of polymer chains at the glass transition, consistent with a more homogeneous network architecture. Furthermore, the integrated area under the E'' curve for the EEA blend was $51,688 \text{ MPa}\cdot\text{min}$, nearly five times larger than the area for the neat epoxy ($10,940 \text{ MPa}\cdot\text{min}$). This confirms that the overall energy dissipation throughout the entire glass transition process is vastly greater in the hybrid system.

3.4.3. Damping Factor ($\tan \delta$)

The damping factor ($\tan \delta$), defined as the ratio of the loss modulus to the storage modulus (E''/E'), quantifies a material's ability to dissipate mechanical energy under cyclic loading. The $\tan \delta$ (damping factor) curves provide critical insight into the glass transition and the homogeneity of the polymer networks. The reinforced epoxy exhibits a tall, sharp $\tan \delta$ peak with a maximum of 1.185 at 101.36°C (Figure 6c). In contrast, the reinforced epoxy/epoxy acrylate (EEA) blend shows a 17% reduction in peak height (max $\tan \delta = 0.9843$) and a slightly lower peak temperature (99.38°C). The reduction in peak height is a key indicator of a more elastic, highly cross-linked network. The EEA blend dissipates

less energy as heat during deformation, behaving in a more “solid-like” manner due to the restrictive nature of the interpenetrating network (IPN) structure.

3.4.4. Cole–Cole Plot

The viscoelastic behavior was further analyzed using a Cole–Cole plot (Figure 6d), which depicts the relationship between the loss modulus (E'') and storage modulus (E'). A Cole–Cole plot is a graphical representation, and it is a plot of the loss modulus (E'') on the y-axis against the storage modulus (E') on the x-axis. Essentially, it is a parametric plot where each data point corresponds to a specific temperature, and the resulting curve visualizes the relationship between the elastic and viscous components of the material's stiffness throughout a transition. The power of the Cole–Cole plot lies in its shape, which provides immediate insight into the homogeneity and nature of the polymer network. A perfectly homogeneous material with a single, sharp relaxation time would produce a perfect semicircle in the Cole–Cole plot. The top of the semicircle represents the point where energy dissipation (E'') is at its maximum during the glass transition. If a system has multiple, distinct phases, such as an epoxy-rich phase and an epoxy-acrylate-rich phase, or interfaces around HNTs, the Cole–Cole plot may show shoulders, distortions, or even multiple arcs. Each distinct arc suggests a different molecular relaxation process associated with a different phase.

The broad, slightly asymmetrical arc is a classic signature of a complex, multi-phase system. In the context of this work, this heterogeneity directly reflects the successful formation of an interpenetrating network (IPN) structure between the epoxy and epoxy acrylate phases. The different chain mobilities and cross-link densities in these two interpenetrated networks contribute to the wide range of relaxation times observed. The presence of well-dispersed halloysite nanotubes (HNTs) further contributes to this behavior. The polymer chains at the polymer–nanotube interface experience different levels of confinement and mobility compared to the bulk polymer, creating additional, distinct relaxation mechanisms that skew and broaden the Cole–Cole arc.

3.5. Differential Scanning Calorimetry (DSC)

The thermal transitions of the prepared blends and nanocomposites were investigated using differential scanning calorimetry (DSC). The thermograms displayed in Figure 7 and the tabulated thermal data in Table 2 reveal significant insights into the glass transition characteristics and thermal stability as a function of blend composition and HNT reinforcement.

Table 2. Thermal profile of epoxy blends and composites: DSC data.

Sample Code	DSC							
	1st Small Transition (Glass Transition Peak T_g)				2nd Small Transition			Degradation Transition
	T_{Onset} (°C)	T_g (°C)	ΔC_p (J/g·°C)	ΔH (J/g)	$T_{2nd-Transition}$ (°C)	ΔC_p (J/g·°C)	ΔH (J/g)	T_{deg} (°C)
E	60.00	79.25	9.348	50.82	164.70	3.706	6.174	410.4
EEA-75/25	71.24	84.73	4.938	11.14	159.25	3.109	2.953	398.7
EEA-50/50	60.42	81.39	5.810	18.44	164.9	3.489	4.602	402.5
EEA-25/75	68.25	82.98	3.551	11.14	163.32	2.843	9.463	392.7
EH	63.85	80.84	7.698	40.22	168.43	3.173	3.927	408.3
EEA-75/25 H	60.17	78.6	3.130	6.042	169.68	2.605	3.200	441.4

The primary glass transition temperature (T_g), identified from the midpoint of the step-change in heat capacity, serves as a key indicator of network mobility and cross-link

density. The neat epoxy (E) exhibited a T_g of 79.25 °C (Figure 7a). With the introduction of the epoxy acrylate phase, the T_g of the blends (EEA series) showed a complex, non-linear dependence on composition. The EEA-75/25 blend displayed the highest T_g at 84.73 °C, indicating a synergistic restriction in chain mobility. This increase is attributed to the formation of an interpenetrating network (IPN) that imposes additional topological constraints on segmental motion. For other compositions (EEA-50/50 and EEA-25/75), the T_g values (81.39 °C and 82.98 °C, respectively) remained higher than the neat epoxy but lower than the EEA-75/25 blend, suggesting the 75/25 ratio achieves an optimal network architecture.

A critical observation is the reduction in the heat capacity change (ΔC_p) at the glass transition for all blends compared to the neat epoxy (e.g., 4.938 J/g·°C for EEA-75/25 vs. 9.348 J/g·°C for E). This parameter is directly proportional to the fraction of mobile chain segments that become activated during the transition. Its value is a powerful indicator of network cross-link density and constraint [54,55]. The significantly lower ΔC_p in the blends strongly suggests the formation of a more densely cross-linked and constrained network, where a larger portion of the polymer is immobilized within the rigid IPN structure, leaving fewer chains free to undergo the glass transition.

The ΔH at T_g 50.82 J/g for neat epoxy indicates a significant degree of physical aging or internal stress relaxation occurring during the glass transition. It suggests that the neat epoxy network, upon cooling from the cure temperature, settled into a non-equilibrium, metastable glassy state with considerable frozen-in free volume or residual stresses. In contrast, all blends exhibit a dramatic reduction in ΔH at T_g (e.g., 11.14 J/g for EEA-75/25). This is a critical finding. The drastic decrease implies that the interpenetrating network (IPN) structure achieves a more relaxed, equilibrium-like glassy state. The mutual constraints imposed by the two interpenetrated networks likely hinder the large-scale molecular rearrangements necessary for physical aging, resulting in a glass with a lower enthalpy state and less energy required for relaxation during the DSC scan. This correlates perfectly with the observed increase in T_g and decrease in ΔC_p , collectively painting a picture of a highly constrained, densely cross-linked network.

The addition of HNTs to the cured networks produced distinct and composition-dependent effects (Figure 7b). In the neat epoxy system (EH), HNTs caused a slight T_g increase to 80.84 °C, consistent with conventional nano-reinforcement, where filler-polymer interactions mildly restrict chain mobility. In contrast, for the optimized IPN system, the HNT-reinforced EEA-75/25-H composite exhibited a significant decrease in T_g to 78.6 °C alongside a further reduced ΔC_p of 3.130 J/g·°C. This apparent plasticization effect, coupled with an even more constrained network (lower ΔC_p), presents a sophisticated picture. This is attributed to the HNTs acting as a compatibilizing interface within the IPN. They may preferentially interact with the epoxy acrylate phase, potentially reducing the interfacial tension between the two interpenetrated networks and creating a slightly more mobile interfacial region, which lowers the overall T_g . However, the drastically lower ΔC_p confirms that the bulk network remains highly rigid, suggesting the HNTs are integral to the IPN, disrupting its cooperative relaxation and leading to a broader distribution of relaxation times—a finding consistent with the broadened $\tan \delta$ and Cole–Cole plot. The addition of HNTs further modulates this behavior. For reinforced epoxy (EH, ΔH at T_g = 40.22 J/g), HNTs cause a noticeable reduction (from 40.22 J/g of ΔH at T_g for neat epoxy E), suggesting they may restrict chain mobility enough to slightly inhibit the aging process. For the EEA-75/25-H composite (ΔH at T_g = 6.042 J/g), the value is the lowest of all, indicating that the combined effect of the IPN and the nanofiller creates the most kinetically constrained and stable glassy network, virtually eliminating detectable enthalpy relaxation.

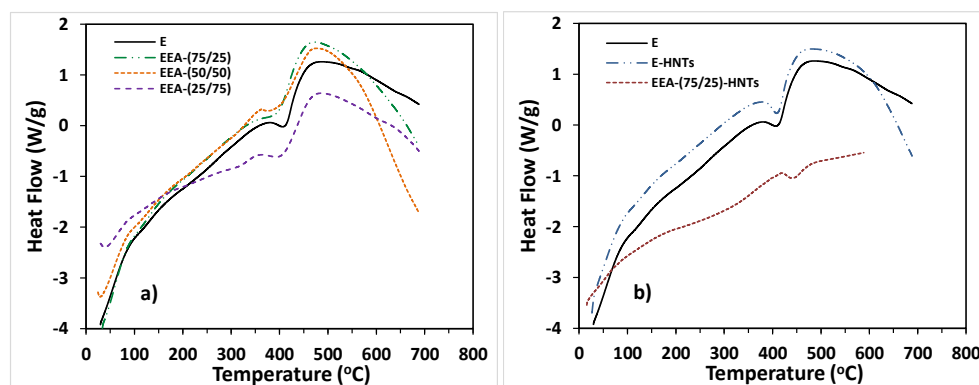


Figure 7. DSC curves for (a) epoxy/epoxy acrylate blends and its (b) nanocomposites.

A small endothermic transition observed between 159 and 170 °C for all samples is a thermal disruption event, indicative of relaxation of residual stresses within the highly cross-linked network. The enthalpy (ΔH) associated with this transition is notably higher for the neat epoxy (6.174 J/g), which likely corresponds to the dissociation of weakly bound, ordered domains (e.g., locally packed bisphenol A segments) or the relaxation of highly constrained, secondary cross-links or chain entanglements that are stable below the main T_g . ΔH reduces significantly for the blend EEA-75/25 (i.e., 2.953 J/g), suggesting that the IPN formation disrupts the long-range order or the specific interactions present in the neat epoxy. The hybrid network's heterogeneous nature may prevent the formation of the same type or extent of ordered structures that melt in this temperature range. Which means the dual-cure IPN system achieves a more complete conversion during the primary cure cycle, leaving less internal stress to relax at elevated temperatures. Interestingly, ΔH increases with the increase in epoxy acrylate contents, indicating that a new type of ordered structure or specific interaction within the acrylate-rich phase or at the interphase develops, which then dissociates endothermically. The addition of HNTs to the EEA-75/25 blend shows a distinct increase in T_{2nd} and reveals the potential of the halloysite nanotubes to stabilize these secondary structures. The strong interfacial interactions between the polymer and the nanotube surface may create new, more thermally robust constrained regions or promote a different mode of local chain packing that requires a higher energy input to disrupt. This bifurcation indicates that while the IPN randomizes the neat epoxy's native order, the HNTs impose a new, nano-confinement-driven order that is even more thermally stable. This demonstrates the nanotubes' role as an active structural element, not just a passive filler. Furthermore, the values of ΔC_p at the 2nd transition are much smaller than ΔC_p at T_g , confirming this is a more localized event involving fewer segments. The general decrease in ΔC_p_{2nd} for blends and composites (e.g., from 3.706 J/g·°C in neat epoxy to 2.605 J/g·°C in EEA-75/25-H) parallels the trend in ΔC_p at T_g . It suggests that the same constraining factors (IPN formation, HNT interface) that reduce the mobile fraction at the main T_g also reduce the number of chain segments capable of participating in this higher-temperature, more localized ordering/disordering process.

The onset of the major degradation transition, observed above 390 °C, provides a measure of thermal stability. Most notably, the thermal degradation stability was profoundly enhanced by HNTs within the IPN. The HNT-reinforced EEA-75/25-H composite showed a dramatic increase in its degradation peak temperature to 441.4 °C, outperforming the neat epoxy (410.4 °C) by over 30 °C and all other samples. This superior performance underscores the synergistic barrier effect of HNTs within the IPN matrix. The nanotubes create a labyrinthine pathway that effectively retards the diffusion of volatile decomposition products, significantly delaying the onset of major weight loss.

3.6. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was conducted to evaluate the thermal stability and degradation behavior of the cured epoxy systems. The key parameters, including characteristic degradation temperatures, mass loss rates, and residual char yield, are displayed in Figure 8, summarized in Table 3, and discussed in detail below.

From thermogravimetric (TG) curves, the onset of thermal degradation, a critical indicator of material stability in high-temperature environments, was assessed through multiple metrics, i.e., initial decomposition ($T_{5\%}$, $T_{10\%}$), T_{onset} , midpoint degradation ($T_{50\%}$), slope of the degradation region (T_{onset} to T_{endset}), and char residue at 600 °C. The temperatures for 5% and 10% weight loss ($T_{5\%}$, $T_{10\%}$) provide a conservative measure of usable thermal stability [56]. The neat epoxy (E) began significant decomposition at $T_{5\%} = 290$ °C (Figure 8a). All modified systems showed a marked improvement. The EEA-75/25 blend increased $T_{5\%}$ to 322 °C, while the EEA-75/25-H nanocomposite achieved the highest value at 352 °C. This 62 °C improvement conclusively demonstrates that the synergistic combination of the epoxy/epoxy acrylate interpenetrating network (IPN) and halloysite nanotubes (HNTs) creates a superior thermal barrier, significantly delaying the initial stages of decomposition. $T_{50\%}$ also shifted from 402 °C for EEA-75/25 to 430 °C for EEA-75/25-H, with a 25 °C improvement because of the addition of HNTs.

The onset (T_{onset}) and endpoint (T_{endset}) temperatures of the primary degradation step, as determined by the tangent method on the TGA curves, are critical parameters that define the thermal operating window and decomposition profile of the polymer networks. The systematic variation in these values provides direct evidence of the structural modifications induced by blending and nanofiller incorporation. T_{onset} marks the temperature at which the polymer network begins to undergo rapid, autocatalytic chain scission, leading to measurable volatile loss. A higher T_{onset} indicates that a greater energy input is required to initiate this irreversible breakdown. Neat epoxy (E) exhibits a T_{onset} of 371 °C, establishing the baseline thermal resilience of the cross-linked DGEBA/anhydride network. Epoxy/epoxy acrylate blends (EEA Series) show a moderate increase in T_{onset} (e.g., 363 °C for EEA-75/25, 368 °C for EEA-25/75). This 5–8 °C enhancement suggests that the interpenetrating network (IPN) structure imparts a modest stabilizing effect, likely by increasing the overall cross-link density and creating a more tortuous path for the initial decomposition products to escape, thereby slightly delaying the onset of rapid weight loss.

The most significant improvements are observed for HNT composites (Figure 8c). The HNT-reinforced neat epoxy (EH) shows a T_{onset} of 381 °C (+10 °C vs. neat epoxy). Remarkably, the EEA-75/25-H nanocomposite achieves a T_{onset} of 401 °C, a substantial 30 °C increase over the neat epoxy, and a 38 °C increase over its unfilled blend counterpart. This dramatic shift is a cornerstone finding. It demonstrates a powerful synergistic stabilization effect: the HNTs, when dispersed within the char-forming IPN matrix, act as exceptional nano-barriers. They physically hinder the diffusion of heat and the outward migration of volatile decomposition fragments, thereby significantly raising the thermal energy threshold required to trigger catastrophic network degradation.

T_{endset} represents the temperature at which the primary degradation event is essentially complete, and the remaining material (char) enters a region of slower, high-temperature oxidative or secondary decomposition. A very similar trend has been seen for T_{endset} , which shows a T_{endset} of 469 °C for EEA-75/25-H and a 19 °C increase over its unfilled blend counterpart, confirming that its residual char residues are more thermally stable, which withstands higher temperatures before undergoing final oxidative breakdown, contributing to the material's overall fire-resistant properties.

The slope of the single-step degradation region in the TGA curve quantifies the overall rate of weight loss. The neat epoxy exhibited the steepest slope (−1.251%/°C). The formation of the IPN structure in the blends resulted in shallower slopes (e.g., −1.021%/°C

for EEA-75/25), indicating a more controlled, gradual decomposition. Notably, while HNTs increased the onset temperature in the EEA-75/25-H composite, the degradation slope ($-1.272\%/^{\circ}\text{C}$) was steeper than its unfilled blend counterpart but less steep than neat epoxy. This suggests a complex kinetic interplay: the HNTs delay the onset (barrier effect), but once degradation initiates in the highly reinforced matrix, it may proceed in a concerted manner. However, the dramatically increased char yield confirms that a significant fraction of the material is converted to a stable residue rather than volatilized.

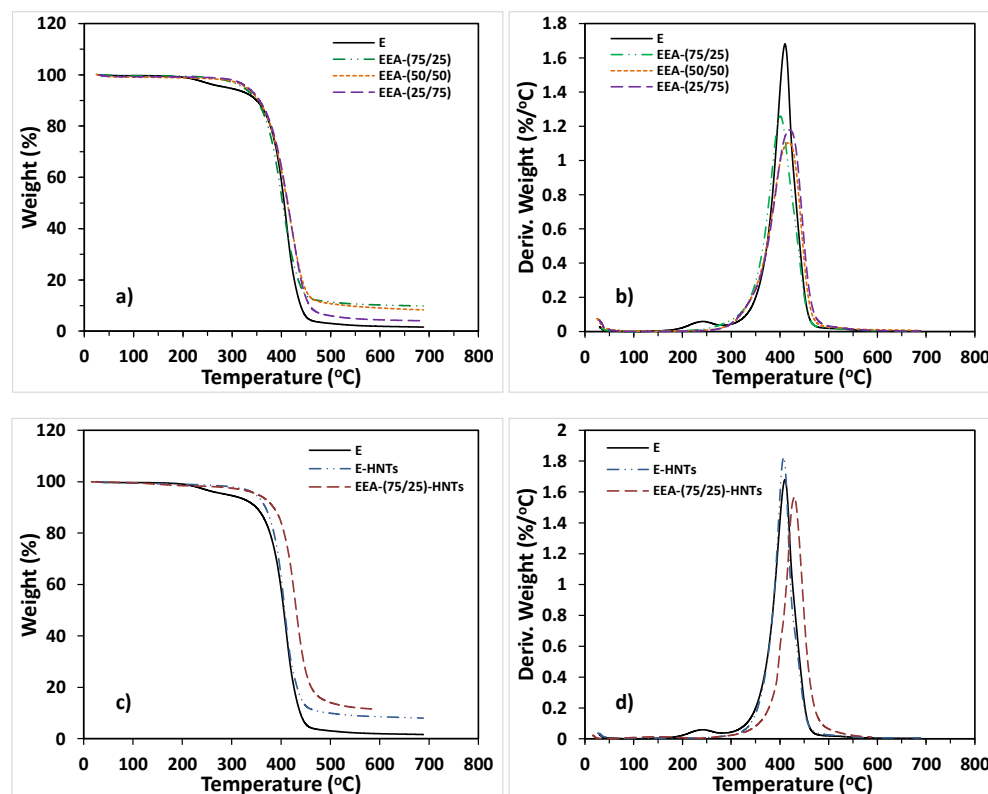


Figure 8. TG and Deriv. TG curves for (a) epoxy/epoxy acrylate blends and its (b) nanocomposites, (c) TG for HNT composite and Deriv. (d) TG curves for HNT composite.

The residual char yield is a vital parameter, indicating the material's propensity for condensed-phase carbonization, which acts as a protective barrier. The neat epoxy left a minimal char residue of 1.92%. The formation of the IPN structure alone substantially increased the char yield (e.g., 10.25% for EEA-75/25), suggesting that the epoxy acrylate phase promotes char formation. This effect was maximized in the HNT-reinforced composite (EEA-75/25-H, 11.50%), demonstrating that HNTs catalyze or synergistically enhance the char-forming ability of the IPN matrix, further contributing to flame retardancy and thermal shielding.

The DTG peak temperature ($T_{\max}$) corresponds to the point of maximum mass loss rate [56]. Figure 8b,d show the DTG curves for epoxy blends and composites. Neat epoxy (E) exhibited a $T_{\max}$ of 410.55°C , while epoxy/epoxy acrylate blends showed a composition-dependent trend. The EEA-75/25 blend has a slightly lower $T_{\max}$ (400.86°C), which may indicate that the initial decomposition event involves a slightly less stable component of the IPN. However, EEA-50/50 and EEA-25/75 showed increased $T_{\max}$ values (417.87°C and 420.00°C , respectively), suggesting that at higher epoxy acrylate content, the network's overall backbone stability improves. Halloysite-reinforced composites clearly demonstrated the synergistic effect of nanotubes in composites. The HNT-reinforced

(EEA-75/25-H) nanocomposite achieved the highest $T_{\max}$ of 429.6 °C, a 19 °C increase over the neat epoxy and a 29 °C increase over its corresponding unfilled blend. This confirms that the HNTs, integrated within the IPN, effectively reinforce the polymer backbone, delaying the temperature at which chain scission kinetics are maximized. The nanotubes likely act as radical scavengers and thermal insulators at the molecular level, requiring higher thermal energy to achieve the same degradation rate. The rate of maximum degradation ($dW/dT_{\max}$) corresponds to the intensity of decomposition. A lower value indicates a less violent, more controlled decomposition process, which is favorable for flame retardancy as it implies slower fuel generation. Neat epoxy (E) exhibited a peak rate of 4.328%/min. While the unfilled blends show similar or slightly higher peak rates, the introduction of HNTs leads to a reduction. The HNT-reinforced neat epoxy (EH) shows a rate of 3.901%/min, and the optimized EEA-75/25-H composite shows 4.200%/min. Although this is a modest reduction, it is significant that this lower peak rate occurs at a much higher temperature (429.6 °C vs. 410.55 °C). This combination—higher temperature but slower peak rate—is a signature of a barrier-controlled degradation mechanism. The HNTs and the forming char layer impede the volatilization of decomposition products, spreading the mass loss over a broader temperature range and reducing the maximum instantaneous release rate.

The slope of the leading edge of the DTG peak, calculated from the baseline before T_{onset} (DTG ~0) to the peak maximum, represents the initial acceleration of the degradation reaction (d^2W/dT^2). A steeper slope indicates a faster transition from stable polymer to rapid, autocatalytic decomposition. Neat epoxy (E) serves as the kinetic baseline, and epoxy/epoxy acrylate blends exhibited a significantly shallower DTG slope compared to the neat epoxy (e.g., the slope for EEA-75/25 is less than half that of neat epoxy). This is a critical finding. It demonstrates that the IPN structure fundamentally alters the degradation kinetics, causing it to accelerate more gradually. The heterogeneous, interpenetrated network likely decomposes in a less cooperative, more sequential manner, as different phases or constrained regions break down at slightly different rates, leading to a broader, less sharp ascent to the peak. The HNT-filled samples show an intermediate slope value—higher than the unfilled blends but still indicative of a controlled process. This suggests that while the HNTs provide immense thermal stability (raising T_{onset} and $T_{\max}$), they also help define a clearer primary degradation step. Once the protective barrier of the nanotubes is surpassed at the elevated T_{onset} , the degradation of the polymer matrix may proceed with a somewhat sharper kinetic profile, albeit at a reduced overall rate (lower peak height) and a much higher temperature.

Table 3. Thermal profile of epoxy blends and composites: TGA data.

Sample Code	TGA									
	DTG Curves					TG Curves				
	$T_{\max}$ (°C)	$R_{\max\text{-deg}}$ (%/min)	Slope_deg (T_{onset} to T_{top}) (%/°C)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	T_{onset} (°C)	T_{Endset} (°C)	Slope_deg (T_{onset} to $T_{\text{End-}}$ set) (%/°C)	Char% at 600 °C
E	410.55	4.328	0.01199	290	350	405	371	451	0.02995	1.92
EEA-75/25	400.86	4.363	0.00522	322	349	402	363	450	0.00149	10.25
EEA-50/50	417.87	4.404	0.00609	329	354	411	366	458	0.00283	9.06
EEA-25/75	420.00	4.695	0.00563	332	355	412	368	461	0.00246	4.44
EH	408.00	3.901	0.00790	348	367	407	381	447	0.00031	8.53
EEA-75/25 H	429.6	4.200	0.00626	352	385	430	401	469	0.00662	11.50

In conclusion, the epoxy/epoxy acrylate blends (EEA series) consistently show higher $T_{5\%}$, $T_{10\%}$, and char yield, with a shallower degradation slope, revealing their synergic IPN effect over neat epoxy. This establishes the IPN structure as inherently more thermally stable and char-forming. HNTs in neat epoxy primarily improve the initial stability (higher $T_{5\%}$ & $T_{10\%}$) and char yield. Optimal synergy of EEA-75/25-H nanocomposite combines all advantages: the highest initial decomposition temperatures ($T_{5\%} = 352\text{ }^{\circ}\text{C}$), a significantly elevated peak degradation temperature ($429.6\text{ }^{\circ}\text{C}$), the highest char yield (11.50%), and a reduced maximum degradation rate. This represents the optimal system where the HNTs effectively reinforce the char-forming, thermally stable IPN matrix. Mechanistically, this set of changes is characteristic of three HNT effects: (i) a physical barrier or “tortuous path” that slows volatilization of degradation products and heat transport; (ii) catalytic/condensing action of the aluminosilicate surface that promotes crosslinking/char formation during pyrolysis; and (iii) enhanced thermal conductivity local to the filler that redistributes heat and delays runaway degradation. The increased char% supports (ii): HNTs are participating in the formation or stabilization of thermally stable carbonaceous residue rather than being inert fillers. Together, these effects explain why the composite resists mass loss to higher temperatures and why the DTG maximum shifts to higher temperatures. The combined effect of HNTs is strongly beneficial for high-temperature applications: the higher $T_{5\%}$, $T_{10\%}$, and $T_{50\%}$, DTG maximum, and larger char suggest improved thermal endurance and enhanced resistance to thermal-oxidative failure—useful for protective coatings, adhesives for elevated temperatures, and thermally demanding structural components. The reduced ΔC_p (observed in DSC analysis) and inferred interphase HNT blends are expected to raise the composite’s modulus (observed in DMA) at service temperatures below T_g , even if the apparent bulk T_g is slightly lower. In short, thermomechanical stiffness at use temperatures and thermal degradation resistance both improve.

3.7. Surface Morphology

The morphology of the halloysite nanotubes (HNTs) was investigated by scanning electron microscopy (SEM) to elucidate the microstructure, fracture behavior, and dispersion state within the optimized epoxy/epoxy acrylate (EEA-75/25) nanocomposite. Iridium was sputter-coated prior to SEM analysis because iridium is an excellent choice for high-resolution imaging, as it forms much finer films than gold and is also used for its non-oxidizing properties.

The SEM micrograph of pristine HNTs (Figure 9a,b) provides additional microstructural detail on the morphology of nanotubes beyond the features discussed earlier, which confirms the characteristic tubular geometry of the nanofiller. HNTs appear as elongated filaments, exhibit a smooth surface morphology, are predominantly discrete, have minimal aggregation, and have an outer diameter distribution ranging from approximately 40 to 90 nm, with lengths varying from several hundred nanometers to over a micrometer, confirming the high aspect ratio of the HNTs. This well-defined, non-aggregated tubular morphology is advantageous for composite reinforcement, as it promotes mechanical interlocking and provides a large surface area for polymer–filler interaction.

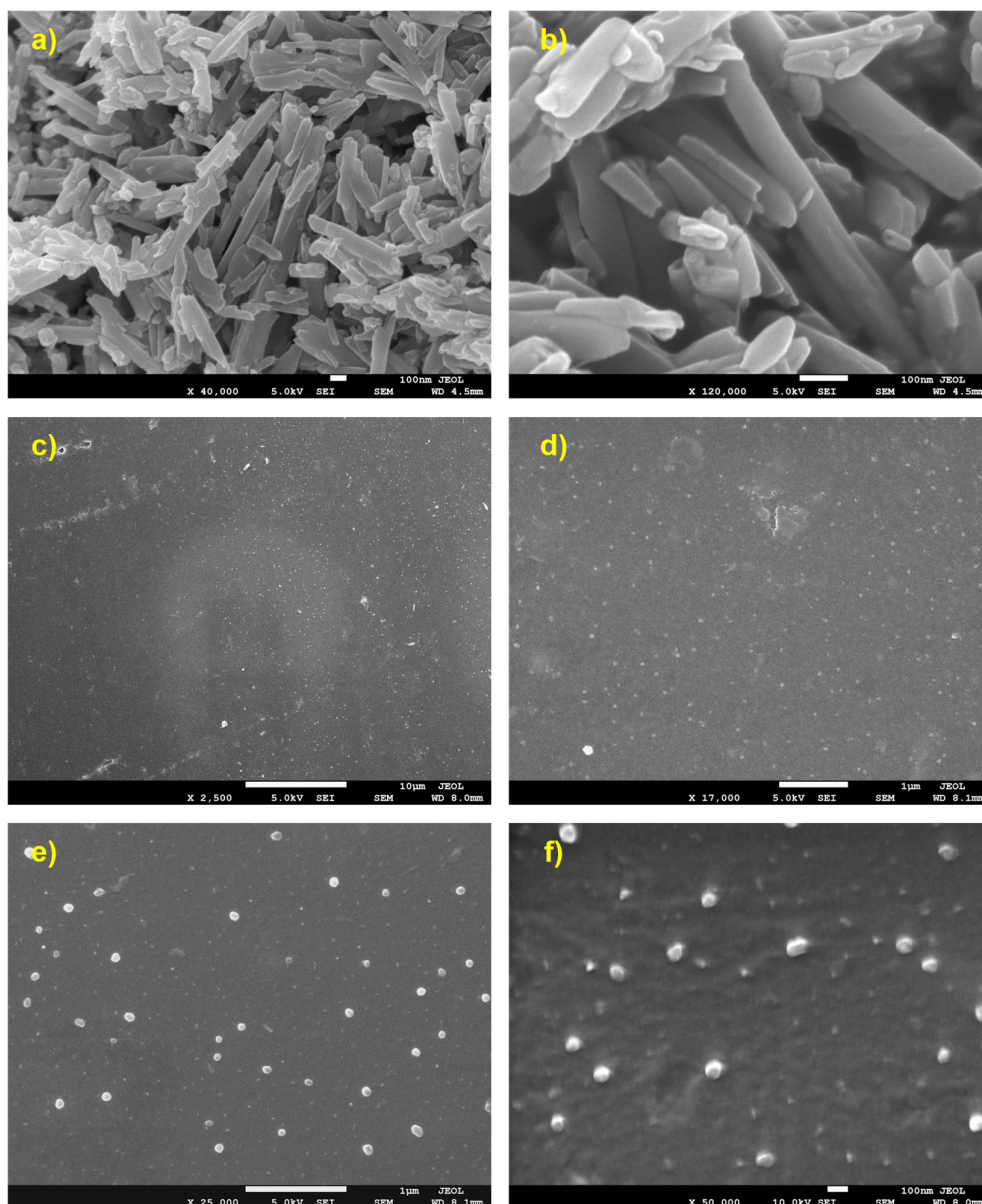


Figure 9. SEM images of (a,b) pristine halloysite nanotubes (HNTs), (c–f) reinforced epoxy/epoxy acrylate blends (2 wt% loading of HNTs, (EEA-75/25)). HNTs are homogeneously dispersed within the cured epoxy matrix.

Figure 9c–f show the surface morphology of the optimized reinforced blend (EEA-75/25-H) with an exceptional state of nanofiller dispersion. The nanotubes are distributed uniformly and homogeneously throughout the epoxy/epoxy acrylate matrix without visible aggregates or clusters, confirming the effectiveness of the dual-step mixing protocol involving mechanical stirring and subsequent ultrasonication. Numerous HNTs are seen with one end protruding from the matrix surface, while the rest of the nanotubes remain fully embedded and wetted by the polymer, creating a nano-textured composite surface. This configuration is a direct indicator of excellent matrix infiltration, chemical compatibility, and robust interfacial bonding. Furthermore, the ends of the nanotubes are fuzzy and blurry. Additionally, the absence of voids or gaps at the polymer–nanotube interface suggests strong physicochemical interactions, likely between the aluminol groups on the HNT surface and the polar functional groups of the epoxy and epoxy acrylate networks.

This uniform dispersion and strong interfacial adhesion form the essential microstructural foundation for the effective stress transfer and property enhancements measured in the nanocomposite.

Figure 10 shows the fracture surface of the EEA-75/25-H nanocomposite. The surface exhibits a rough and tortuous morphology, which is a direct indicator of enhanced fracture toughness and crack-path deflection. The well-dispersed HNTs act as rigid obstacles in the path of a propagating crack, as observed in an intact HNT showing a visible lumen. The crack front is forced to deviate around the nanotubes, significantly increasing the fracture surface area and consuming more energy. These observations explain enhanced energy dissipation inferred from the higher storage modulus and large integrated E'' area. Secondly, some nanotubes can be seen spanning micro-cracks, a mechanism known as crack bridging. These bridging nanotubes apply closure stresses on the crack faces, effectively reducing the stress intensity at the crack tip and hindering further propagation. Thirdly, the nanotubes' pull-out features were seen in SEM images. Several HNTs are observed protruding from the fracture surface, with corresponding cavities left behind in the matrix. This pull-out mechanism is a clear signature of effective reinforcement because a combination of debonding and frictional pull-out converts mechanical work into interfacial friction and polymer chain stretching, consistent with DMA findings. It indicates that the interfacial shear strength is optimized—sufficiently strong to transfer load, yet not so strong as to cause nanotube fracture, allowing the pull-out process to absorb substantial energy through friction.

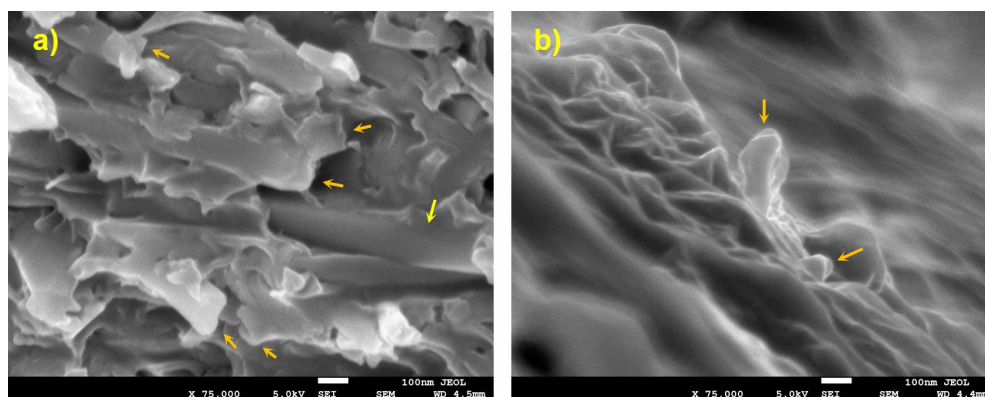


Figure 10. SEM images of the fractured surface of reinforced epoxy/epoxy acrylate blends (2 wt% loading of HNTs, EEA-75/25) at two different locations (a), and (b) showing the fracture morphology. Brown arrows indicate HNTs firmly pinned and wetted by the matrix resin, revealing details of nanotubes' dispersion and interfacial adhesion. While yellow arrows point to nanotubes pulled out during fracture, evidencing energy dissipation through pull-out mechanisms.

3.8. Energy-Dispersive X-Ray Spectroscopy (EDX)

The chemical identity and purity of the nanofiller are paramount, as they directly dictate interfacial compatibility and reinforcement efficacy. Energy-dispersive X-ray spectroscopy (EDX) was performed on the pristine halloysite nanotubes and their reinforced epoxy/epoxy acrylate nanocomposite to (a) confirm the chemical identity of HNTs and (b) use this information to investigate whether the HNTs have been wetted by the epoxy/epoxy acrylate matrix as initially observed in SEM analysis. Figure 11 shows the EDX spectrum of pristine HNTs. The quantitative analysis yielded an atomic composition of O (55.8%), Si (22.5%), and Al (21.7%). This composition aligns closely with the idealized empirical formula for halloysite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$, which contains equal proportions of Al and Si coordinated within alternating tetrahedral–octahedral layers [57,58]. For the

anhydrous ($7\text{\AA}$) form, the molar mass of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ through stoichiometric calculation comes to 258.16 g/mol, and the theoretical weight % comes to O (55.8%), Si (21.8%), and Al (20.9%). The near-perfect match, particularly for oxygen (55.8% measured vs. 55.8% theoretical), and the consistent Al:Si ratio close to 1:1 ($21.7:22.5 \approx 0.96$) provide definitive chemical confirmation that the nanofiller used is high-purity aluminosilicate halloysite, establishing a reliable chemical basis for interpreting its successful integration and multi-functional role within the hybrid polymer network. Furthermore, the consistent composition ensures batch-to-batch reproducibility, a critical factor for scalable manufacturing.

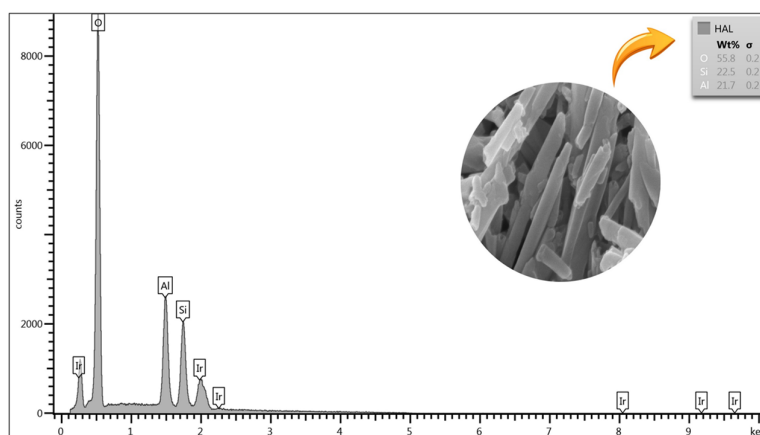


Figure 11. Energy-dispersive X-ray spectroscopy (EDX) of pristine HNTs.

To probe the nature of the polymer-nanofiller interface at the microscale, energy-dispersive X-ray spectroscopy (EDS) was performed on the cured EEA-(75/25)-H nanocomposite at two distinct locations (Figure 12). A comparative spot analysis between a HNT-enriched region (Spot 2) and a HNT-depleted matrix region (Spot 1) provides direct chemical evidence of interfacial integration. The EDX spectrum from a HNT-depleted matrix region (Spot 1, no area of visible HNT) yielded an elemental composition of C (85.3%) and O (14.7%). This composition is characteristic of the cured organic polymer matrix, consisting primarily of the hydrocarbon backbones of DGEBA epoxy and epoxy acrylate, along with oxygen originating from ether, ester, and hydroxyl groups formed during the curing reactions. The near absence of silicon (Si) and aluminum (Al) at this spot confirms the efficacy of the dispersion protocol, indicating that the HNTs are distributed as discrete entities rather than forming a pervasive, micron-scale aggregate network that would otherwise contribute a background signal of inorganic elements. In contrast, the analysis performed directly on a halloysite nanotube feature embedded in the matrix (Spot 2) revealed a markedly different composition: C (73.0%), O (25.3%), Al (1.0%), and Si (0.7%) compared to pristine HNTs. The presence of Al and Si with ~1:1 composition—the hallmarks of the aluminosilicate HNT structure—serves as unambiguous proof of the nanotube's presence and its successful incorporation into the composite. This reveals a dominant carbon signal alongside oxygen, aluminum, and silicon. This profile starkly contrasts with the pristine HNT composition, where carbon is absent. Here, (a) the emergence of a strong carbon peak vs. pristine HNTs (73.0% vs. 0%) and concurrent decrease in oxygen content (from 55.8% to 25.3%), and (b) reduced carbon content (from 73.0% to 85.3%) and increased oxygen contents (from 14.7% to 25.3%) vs. the epoxy-based matrix evidently demonstrate that the halloysite nanotubes are thoroughly encapsulated and wetted by the epoxy/epoxy acrylate matrix. The reduced intensity of the Al and Si signals, relative to their pristine state, reflects the filler and the matrix dilution effect and further witnesses that the HNTs are not merely physically lodged on the surface but are intimately embedded within the

matrix. The polymer has penetrated and adhered to the nanotube surface, effectively masking its native elemental signature. This is a clear spectroscopic signature of excellent interfacial adhesion and matrix infiltration.

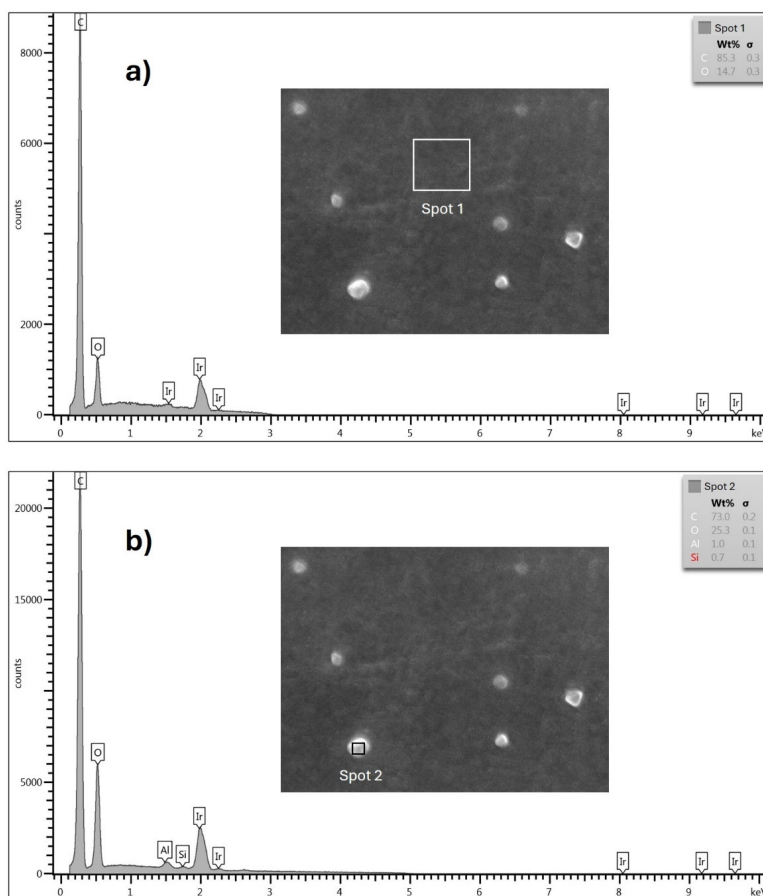


Figure 12. Energy-dispersive X-ray spectroscopy (EDX) of reinforced epoxy/epoxy acrylate blends (2 wt% loading of HNTs, EEA-(75/25)) (a) area without nanotubes; (b) area spotted on nanotubes.

Thus, the clean polymer signature at Spot 1 and the hybrid signature at Spot 2 confirm a homogeneous dispersion where nanotubes are isolated and fully integrated into the matrix. The altered C/O ratio at the interface resulting in the mixed inorganic–organic signal from an individual nanotube is direct proof of excellent wetting and the formation of a contiguous polymer–filler interface with nanoscale intimacy. This strong physical interface is the foundation for effective stress transfer, explaining the observed enhancements in DMA properties.

The performance of the optimized HNT-reinforced epoxy/epoxy acrylate IPN nanocomposite demonstrated a significant advancement when benchmarked against contemporary epoxy nanocomposites. For instance, the incorporation of 2 wt% HNTs yielded a 147% increase in storage modulus, which substantially surpasses the enhancements reported for similar low loadings of carbon-based nanofillers (e.g., 17–31% for 0.4 wt% MWCNTs, GNPs, or GO) [59], functionalized silicates (e.g., 44% for 5 wt% montmorillonite) [60], or pristine halloysite epoxy composites (48% for 1 wt% of HNTs) [8]. Furthermore, the 62 °C increase in the 5% weight loss temperature (T_5) represents a dramatic improvement in thermal stability, eclipsing the modest gains (typically 10–30 °C) observed for nanocomposites based on silicides [61], functionalized clays [62], or mesoporous silica (SBA-15) [63]. Critically, these property enhancements are achieved without

the complex surface functionalization, solvent-intensive processing, or optical opacity often associated with carbon nanotubes, graphene, or metal oxides. This work establishes that the strategic combination of a tailored epoxy/epoxy acrylate IPN matrix with naturally abundant HNTs creates a nanocomposite that outperforms many state-of-the-art systems in both mechanical reinforcement and thermal resilience, while maintaining a simple, scalable, and solvent-free fabrication route.

HNTs were incorporated not as passive fillers but as active, multifunctional components. Their role is tripartite: as mechanical reinforcers, compatibilizing agents, and thermal stabilizers. The exceptional thermal and mechanical performance of the HNT-reinforced epoxy/epoxy acrylate nanocomposite is fundamentally rooted in the unique chemical and structural architecture of halloysite nanotubes, which facilitates superior interfacial bonding with the polymer matrix. Structurally, HNTs are a 1:1 aluminosilicate clay with a stoichiometry of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$, arranged in a curled multiple-layered, hollow, tubular structure consisting of (a) a tetrahedral sheet of siloxane (Si-O-Si) that constitutes the outer surface, imparting low surface energy and chemical inertness, while (b) an alumina octahedral sheet constitutes the inner surface of nanotubes. The rolling of these layers into a tubular shape is primarily due to the lattice mismatch and strain between the larger silica tetrahedral sheet and the smaller alumina octahedral sheet [8,49]. This configuration yields two primary types of hydroxyl (-OH) groups: (a) inner-surface hydroxyls, located on the shared plane of the octahedral sheet, and (b) interlayer hydroxyls, situated on the unshared plane of the tetrahedral sheet [8,45,49,64]. Thus, the exposed hydroxyl groups are present at the ends, edges, and inside the lumen of HNT, with only a limited number of silanol (Si-OH) sites accessible on the exterior (Figure 13). This results in a chemically asymmetric surface: a relatively hydrophobic, low-energy outer shell and a hydrophilic, reactive interior lumen and tube edges rich in aluminol (Al-OH) and silanol groups. This unique chemical anisotropy is fundamental to their interaction with polymer matrices and has important implications for interfacial chemistry, as the reactive sites are strategically positioned to facilitate bonding. These confined hydroxyl-rich regions (Al-OH and Si-OH groups) at the tube edges and defects can engage in strong hydrogen bonding with the hydroxyl (-OH) and ether (-C-O-C-) groups generated during epoxy ring-opening with the anhydride hardener, as well as with the ester (-COO-) groups of the epoxy acrylate. They can participate in the epoxy-anhydride curing reaction, effectively covalently bonding the nanotube to the growing three-dimensional network. This transforms the HNTs from passive fillers into integral, cross-linked components of the thermoset matrix, creating a robust organic-inorganic hybrid network. This explains the dramatic 147% increase in storage modulus (E') and 180% increase in loss modulus (E'') at 50 °C. The IPN matrix provides a stiff, constrained base, while the HNTs act as nanoscale crack arrestors, synergistically improving strength.

The HNTs act as superior heat sinks and radical scavengers, while the strong interface prevents debonding and the formation of easy diffusion pathways for volatiles, as evident from the significantly improved thermal performance of IPN-nanocomposites (i.e., elevated glass transition region, significant reduction in the heat capacity change ΔC_p and ΔH , increased onset and degradation temperature, and increased char%). SEM and EDX analysis further provided direct visual evidence of the HNTs' wetting with epoxy/epoxy acrylate matrix. The homogeneous dispersion and the clear mechanisms of nanotube pull-out and crack bridging confirm effective stress transfer from the matrix to the high-strength nanotubes.

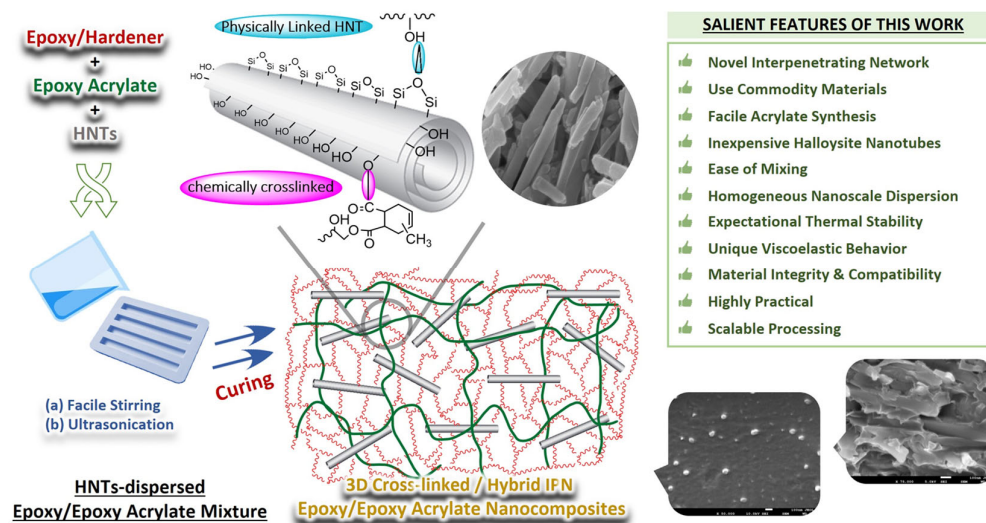


Figure 13. Schematic illustration of the proposed physical and chemical interactions between halloysite nanotubes (HNTs) and the epoxy/epoxy acrylate matrix, highlighting key interfacial mechanisms and the main performance features achieved in this work.

This work establishes a versatile and scalable strategy for engineering high-performance thermoset nanocomposites with markedly improved thermal stability and mechanical performance, highlighting their applicability in advanced structural and engineering contexts. A key feature of the methodology is the conversion of the base epoxy resin into an acrylate derivative to prepare an epoxy modifier that retains a chemically compatible backbone, facilitating miscibility and interphase continuity when blended with the parent epoxy. This structural similarity promotes cohesive network development and enhances overall integrity of the hybrid matrix. Advantageously, this approach utilizes the commodity materials, combined with the use of inexpensive and environmentally benign halloysite nanotubes, to create a synergistic interpenetrating network (IPN) through a simple, solvent-free mixing process. The resulting nanocomposites exhibit exceptional thermal stability and unique viscoelastic properties. Most interestingly, this methodology does not involve any specialized chemistry or procedure but rather utilizes just a facile mixing method, which develops highly uniform and homogeneously dispersed nanocomposites. The dual-step protocol (mechanical stirring and bath sonication) is inherently scalable. Mechanical stirring is standard in industrial resin preparation, and bath or horn ultrasonication can be scaled for larger volumes. HNTs also preserved the optical clarity of reinforced blends, contrasting sharply with the complete opacity induced by other nanofillers (e.g., CNTs), offering a distinct advantage for applications where optical clarity is desirable. The reported approach provides a highly practical and industrially viable pathway to advanced materials for demanding engineering applications.

4. Conclusions

This work focused on the synthesis of an epoxy acrylate as a modifier and the development of halloysite nanotube-reinforced blends based on epoxy/epoxy acrylate resin. The successful synthesis of epoxy acrylate resin was confirmed by ^1H NMR spectra and FTIR spectroscopy, which showed the complete consumption of starting material and the emergence of characteristic acrylate vinyl proton signals at 6.44, 6.16, and 5.87 ppm in the product, confirming the presence of the polymerizable functional group. These results demonstrate the efficient ring-opening esterification of the epoxy resin with acrylic acid. A series of blends at varying weight ratios of epoxy/epoxy acrylate (75/25, 50/50, 25/75)

was prepared and optimized using dynamic mechanical analysis (DMA) for the best viscoelastic performance. Analysis of the stress–strain behavior revealed that the blend containing 25 wt% epoxy acrylate in epoxy resin (EEA-75/25) exhibited the highest mechanical strength among all tested formulations. This composition was therefore selected as the optimal matrix for subsequent HNTs reinforcement and comprehensive characterization. The DMA of the HNT-reinforced epoxy/epoxy acrylate blend achieved a superior synergy of properties, exhibiting a dramatic increase in storage modulus (E') of 147% in glassy state stiffness with a unique pre-transition stiffening effect and a 180% increase in loss modulus (E'') at 50 °C. The IPN matrix provides a stiff, constrained base, while the HNTs act as nanoscale crack arrestors, synergistically improving strength. The nanocomposite exhibits a 62 °C increase in $T_{5\%}$, a 19 °C increase in the primary DTG peak temperature ($T_{\max}$), and a char yield of 11.50%—nearly six times that of neat epoxy. This multifaceted enhancement is attributed to a superior barrier mechanism. The well-dispersed, high-aspect-ratio HNTs create a labyrinthine “tortuous path” within the IPN matrix, dramatically slowing the diffusion of heat and volatile decomposition products. Furthermore, they likely catalyze the formation of a more stable, silicate-reinforced char layer that acts as a protective shield, delaying both the onset and the progression of thermal degradation. The homogeneous dispersion and the clear mechanisms of nanotube pull-out and crack bridging confirm effective stress transfer from the matrix to the high-strength nanotubes.

In conclusion, this work establishes a versatile and effective strategy for designing high-performance thermoset nanocomposites with synergistically enhanced thermal stability and mechanical properties while preserving optical clarity, unlocking their significant potential for advanced engineering applications. Despite the promising results, future studies could focus on exploring varying nanotube loadings, evaluation of additional technological tests, long-term durability, moisture resistance, etc. Finally, while the simple mixing method is a strength for scalability, a techno-economic and lifecycle analysis would be valuable for assessing commercial viability. Nevertheless, the demonstrated approach shows strong potential for applications in thermally stable and durable coatings, structural adhesives, lightweight composite systems, automotive components, and high-performance composite structures.

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Abbreviations

The following abbreviations are used in this manuscript:

CNTs	Carbon nanotubes
DGEBA	Diglycidyl ether of bisphenol A
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DTG	Derivative thermogravimetric analysis
E	Epoxy
E'	Storage modulus
E''	Loss modulus
EA	Epoxy acrylate
EDX	Energy-dispersive X-ray spectroscopy
EEA	Epoxy/epoxy acrylate blends
FTIR	Fourier-transform infrared
HNTs	Halloysite nanotubes
$^1\text{H NMR}$	Proton nuclear magnetic resonance
IPNs	Interpenetrating polymer networks
$R_{\text{max-deg}}$	Maximum rate of degradation
SEM	Scanning electron microscopy
T_{deg}	Degradation temperature
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
T_{max}	Temperature at the maximum degradation rate
XRD	X-ray diffraction
ΔC_p	Heat capacity changes
ΔH	Enthalpy change

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