**New nanocomposites based on poly(benzoxazine-co-epoxy) matrix reinforced by novel graphene single and mixed blend fillers**

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# **Abstract**

We report new nanocomposites with poly(benzoxazine-co-epoxy) matrix reinforced with 1wt% graphene. Curabox 24-111, a benzoxazine resin was copolymerised with Epilok 60-566, a mixture of epoxy resins. Copolymerization was also carried out in the presence of different graphene powders namely Nanene-001 and Nanene-002, used as single fillers and as mixture (relative weight ratio 70:30 or 30:70). DSC results showed the addition of either single filler caused a delay in polymerisation and an increase in the exothermic peak temperature of the curing reaction with a related reduction in *ΔHTotal.* compared to the neat copolymer*.* Copolymerisation showed a 38% reduction and 24% increase in tensile modulus (E) compared to the neat polybenzoxazine and epoxy polymer, with a respective 18% and 30% reduction in tensile strength (TS). Nanocomposites with 0.7wt% Nanene-002 + 0.3wt% Nanene-001 showed the highest increase of 35% in TS, a 1.6% reduction in E and 36% increase in elongation at break (EB) compared to the neat copolymer matrix. Samples with 1wt% Nanene-001 showed the largest reduction of 21% in E, a 27% increase in TS and a 45% increase in EB. Additionally, TGA thermographs showed a 22℃ increase in the onset of degradation (300℃ to 322℃) improving the materials thermal stability.

**Keywords**

Graphene; Benzoxazine; Graphene Nanocomposites; Differential Scanning Calorimetry; Thermogravimetric Analysis; Mechanical Properties.

**1. Introduction**

There is a need for further lightweighting of transport vehicles for aerospace, automotive, construction and military aiming energy saving and net zero emissions. Polymer-matrix nanocomposites are a class of materials, including thermoplastics (1), (2), (3), (4), (5), (6) and thermosets, researched and developed for aerospace and ballistic applications (7), (8), (9), (10), (11) construction and structural applications (12), (13), (14) and successfully used to replace heavier metal components (15), (16), (17), (18), (19), (20). In these systems, the polymer matrix (a thermoplastic or a thermoset) is combined with one or more reinforcing agents. Reinforcing materials evolved over time from micro to nano-fillers providing higher surface area and interaction with the matrix, resulting in better performance at lower weight loading. More recently, graphene and related materials (GRMs) have attracted significant attention in academia and many industry sectors as excellent nanofillers (21), (22), (23), (24).

Benzoxazines (BOZs), also named polybenzoxazine (PBOZs) precursors, form a relatively new class of thermosetting addition-cured phenolic resins, being developed, and extensively studied progressively more in recent years. BOZs possess many desirable characteristics such as close to zero volumetric shrinkage or expansion on curing (polymerisation and crosslinking) (21) and give PBOZs with excellent mechanical properties (25), high char yield on decomposition (22), low fire-smoke toxicity (FST), low water absorption (26), excellent resistance to both chemicals and UV light, and high glass transition temperature (Tg) with a relatively low cross-linking density (22). However, there are drawbacks associated with their use, e.g. high curing temperature (200ºC or higher), difficulty in processing and brittleness of the prepared PBOZs (27), (28).

It has been suggested that copolymerisation of BOZs with other thermosetting resins (29), (30), (31), (32), (33) with the addition of reinforcing agents, such as inorganic fillers (34), (35) or carbon fibres (36), (35) can overcome the shortcomings of neat BOZs. Study of curing of BOZ-graphene oxide (GO) which contained 1wt% GO showed a maximum curing rate 14min earlier than that of the neat resin (22). More recently graphene nanofillers have gained popularity on account of their exceptional mechanical and thermal properties (37), (23).

Curing studies of various BOZ resins has shown great potential in reducing the process time and the energy required (21), (22). It is reported in ref (26) that an increase in the isothermal cure temperature results in a substantial reduction in vitrification time and an increase in the degree of cure. At curing temperature 170°C the degree of cure was 80% while at 210°C the value was 99%.

In recent years the improvements in the mechanical and thermal properties of neat PBOZ and PBOZ-epoxy (EP) copolymer systems have been investigated using a range of fillers as reinforcement (38), (27), (39). It is reported in ref (38) that using an EP, and a biobased BOZ resin doped with boron graphene (BG), at EP 85wt%, BOZ 13wt% and BG 2wt%, showed a decrease of 48% in the curing peak heat release and an increase in impact strength of 22%. Additionally, the incorporation of the BOZ and BG was shown to increase Tg by up to 12%, improve the flame retardancy and improve the thermal stability compared to the neat EP system material. Novel materials that exhibit improvements in mechanical and thermal performance, as well as a reduction in energy required for manufacture would be in high demand in the many industries stated.

The reported work involves the development of a new polymermatrix by copolymerisation of Curabox 24-111, a PBOZ precursor based on Bisphenol-A, aniline, and formaldehyde, with Epilok 60-566, a mixture of EP resins. The curing of BOZ and EP has been shown an increase of cross-linking density and Tg (29), (40), (35), (41), (30), (42). This matrix was then reinforced with the use of two nanofillers, namely Nanene-001 and Nanene-002. Mechanical testing was extended to include two novel mixed blend graphene fillers. A good quality uniform dispersion was achieved with the use of toluene as a solvent medium which was evident from mechanical testing.

**2. Experimental**

## **2.1 Materials**

Bisphenol-A based BOZ resin (Curabox 24-111) and the low viscosity EP resin Epilok 60-566 were obtained from Bitrez Group Limited (UK). The Curabox 24-111 is a PBOZ precursor, based on bisphenol A, aniline, and formaldehyde. According to the manufacturer after thermal curing the prepared PBOZ has a tensile modulus (E) of 4.6 GPa, tensile strength (TS) of 55 MPa and a 2% elongation at break (EB). The Epilok 60-566 when cured with an amine e.g., Curamine 32-494 curing agent at 100:30 wt/wt shows an E of 2.3 GPa, TS of 65 MPa with a 5% EB. In the present work only the Epilok 60-566 was used without amine.

Two different graphene powders were supplied by Versarien namely Nanene-001 and Nanene-002. Nanene-001 is a high quality few-layer graphene powder with D50 less than 4 layers and D50 lateral size x: 1.46μm y: 1.12μm. Nanene-002 is a graphene nanoplatelet powder with large lateral dimensions, D50 x: 2.16μm y: 1.78μm and D50 less than 14.5 layers. Toluene (C7H8) CAS: 108-88-3 with laboratory purity grade was used as a solvent medium for Nanene-002: Nanene-001 dispersion prior to introduction to the BOZ-EP blend. A high temperature silicone (HTS) from DWR plastics UK was used to manufacture the specimen moulds for tensile tests. The use of HTS eliminated the requirement for any release agent, its flexibility enabled the easy release of samples from the mould.

## **2.2 Nanocomposites development and manufacture**

The weight ratio of BOZ-EP resins used was 50:50, 80g of each resin was used for a standard 8 sample batch and was chosen due to its low viscosity and the increased processability, when compared to other studied ratios. The miscibility of the two used resins allowed the successful copolymerisation (curing) of resins.

Attempts were made first to disperse graphene powders directly into the BOZ-EP resins solution, using a mechanical stirrer which produces high shear forces. However, the samples prepared did not show any increase in mechanical properties most probably due to non-uniform dispersion of graphene powders in the viscous resins and formation of graphene agglomerates.

To produce a more uniform dispersion the graphene powders were first dispersed in 25ml of toluene and placed in an ultrasonication bath for 25 mins at room temperature (RT). The resin solution was weighed prior to the addition of the graphene-toluene solution to provide a base weight for confirming complete removal of the solvent, this solution was then added to the resin’s solution (Figure 1). High shear mixing was used to remove the toluene over incremented range of 500rpm – 1000rpm. The combined solution, toluene-free was then placed in a vacuum chamber to fully degas before introduction to the moulds. The amount of toluene used is just a fraction of that required to pre-solvate Curabox 24-111. Using toluene as a solvent medium optimised the dispersion of GRM’s and substantially increased the mechanical properties compared to shear mixing graphene powders directly into the neat resins.

**2.3 Characterisation by DSC**

DSC scans of the studied materials were carried out using a DSC Q10 from ΤΑ Instruments. Samples ~20-30mg were weighted and sealed into aluminium hermetic DSC pans. The sample pan was then put in the DSC cell previously maintained at RT. All DSC runs were carried out under N2 atmosphere. Non-isothermal scans of BOZ, EP, BOZ-EP resins and BOZ-EP-graphene nanocomposites were recorded from RT 20ᵒC up to 450℃ at heating rate 2℃/min. An isothermal scan was performed on BOZ-EP resins at 180ᵒC for 2 h and 200ᵒC for 2 h followed by cooling the sample back to RT; then a dynamic run was carried out at a heating rate of 10ᵒC/min up to 450ᵒC.

**2.4** **Thermogravimetric Analysis**

Samples for thermogravimetric analysis (TGA) were selected and prepared from the tensile samples after mechanical testing. The thermal stability of the single PBOZ and EP polymers, PBOZ-EP copolymer and graphene nanocomposite systems were investigated by TGA using a TGA55 thermogravimetric analyser from TA Instruments. Measurements were taken from 20ᵒC to 850ᵒC at a heating rate of 10ᵒC/min under N₂ flow.

**2.5 Tensile testing**

Tensile tests were performed using a universal testing machine Zwick Roell Z010 with a load cell of 10kN at RT with a crosshead speed of 5mm/min. Moulds were manufactured for the dog bone shape specimens using HTS eliminating the need for any additional release agent whilst providing superb dimensional stability with just 0.08% shrinkage on curing. Tensile samples were produced following the methodology shown in Figure 1. The curing schedule followed was heating at 180℃ for 2 h then further heating at 200℃ for a further 2 h.

**Diagram

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**Figure 1.** Preparation of BOZ-EP copolymer and BOZ-EP-Graphene samples for DSC characterisation and cured PBOZ-EP, PBOZ-EP-Graphene for TGA and tensile testing.

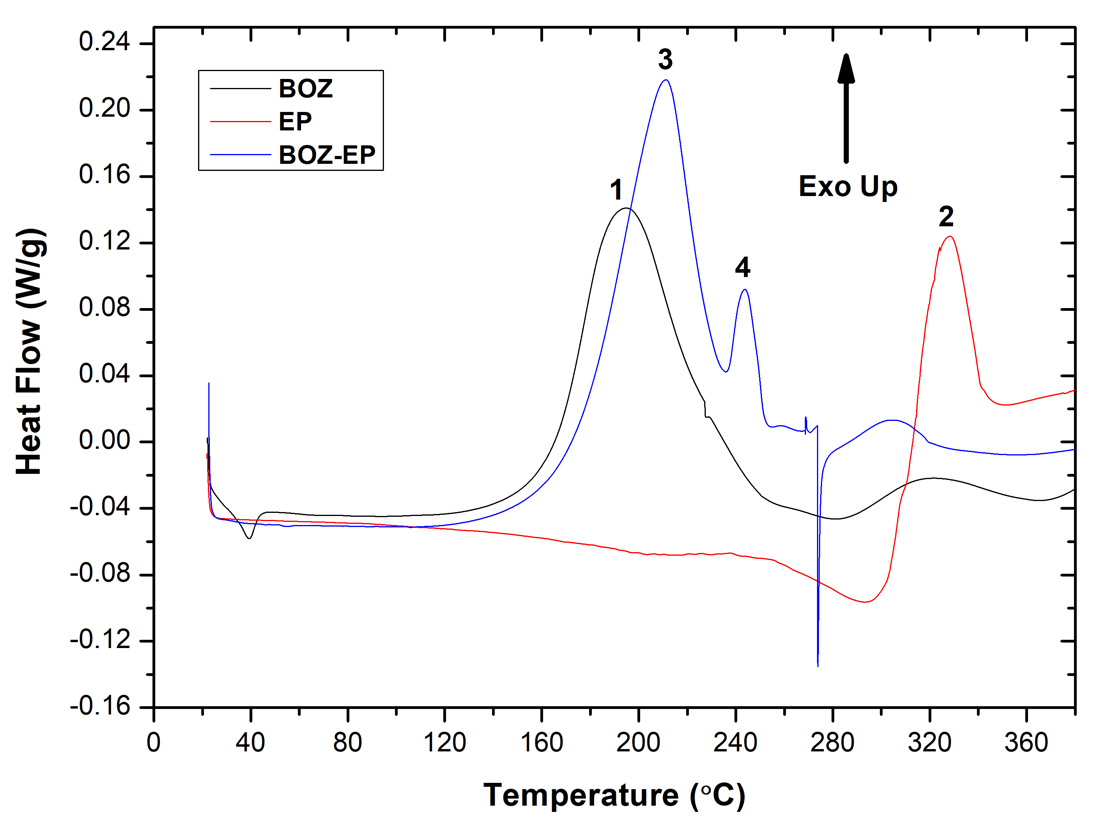
**2.6 SEM Characterisation**

SEM imaging was conducted using a Hitachi S3000-N. Samples were submerged in liquid nitrogen and shattered. These were mounted on an aluminium SEM specimen stub using carbon adhesive discs; stubs and carbon adhesives purchased from Agar Scientific, UK. An approximate 8nm sputter coat was applied using an Agar Scientific AGB7340 Manual Sputter Coater with a gold/palladium target.

# **3. Results and Discussion**

**3.1** **Curing investigation by dynamic DSC**

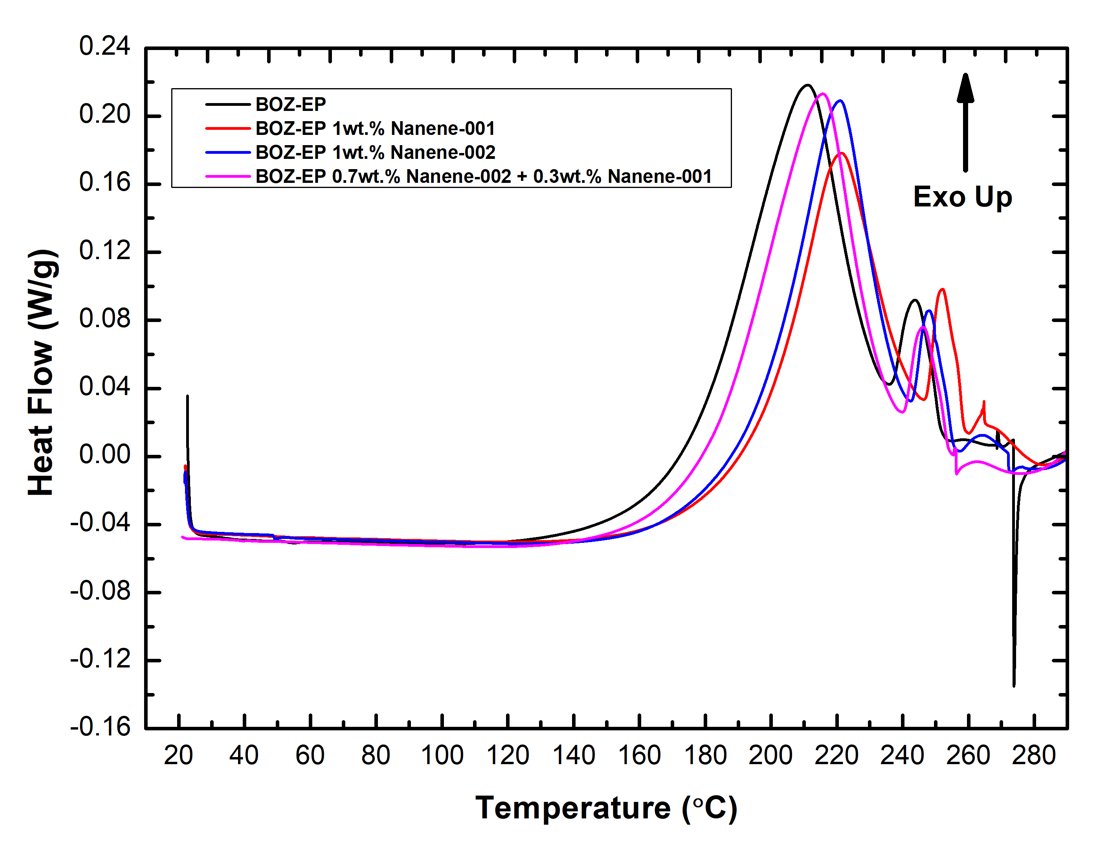
Figure 2 shows the DSC thermographs of BOZ Curabox 24-111, EP Epilok 60-566 and BOZ-EP resins recorded in the temperature range 20 up to 450℃ at a heating rate of 2℃/min. The initial cure temperature (Tinit), the peak maximum temperature (Tmax), final (Tfinal) and Tfinal -Tinit for all studied materials are summarised in Table 1. The Tmax corresponds to the temperature with the maximum curing rate dα/dt (min-1) where α is the degree of conversion. It can be seen in Figure 2 that both resins exhibit two distinctive exothermic curing peaks. It is therefore expected that the curing reaction of BOZ-EP consists of a minimum of two curing stages. The neat BOZ shows an endothermic peak at 40ᵒC which is the melting of the resin and one exothermic symmetrical curing peak starting at 125℃ up to 281℃ (labelled as peak 1 in Figure 2), revealing that the curing process follows a single kinetics mechanism attributed to the polymerisation of BOZ via the heterocyclic ring opening. The neat EP shows an exothermic peak starting at 293℃ and ending at 351℃ (labelled as peak 2), which is due to homo-polymerisation of the EP forming an ether link as similarly reported in Ref (41). The copolymerisation of BOZ with EP shows a non-symmetrical exothermic peak (labelled as peak 3) starting at 128℃ up to 256℃ which can be deconvoluted into two Lorentzian peaks. The first peak is due the homopolymerisation of BOZ; the phenolic hydroxyl groups generated by thermal curing of the BOZ resin were reported (41) to function as a hardener for EP polymerization. Therefore, for the second exothermic peak it was speculated to be the possible reaction corresponded to the side reaction, such as etherification reaction between a hydroxyl group of polymerized BOZ resin and an epoxide to form an ether bond and a new formed hydroxyl group (41). An additional peak is observed in the BOZ-EP at 244℃ (labelled as peak 4), which is most probably due to the homopolymerisation of EP occurring at lower temperature in the reaction mixture BOZ-EP than in EP alone.

**Figure 2.** Non-isothermal DSC of the individual PBOZ and EP systems, PBOZ-EP copolymer at a heating rate of 2℃/min, under N₂ flow, showing exothermic peaks of the curing reactions.

**Table 1.** Characteristic temperatures of curing for the systems under study obtained under non-isothermal conditions at a heating rate of 2℃/min

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Sample** | ***T*init (°C)** | ***T*final**  **(°C)** | ***T*final-*T*int**  **(°C)** | ***T*peak-1**  **(°C)** | ***T*peak-2**  **(°C)** |
| BOZ | 125 | 281 | 156 | 195 | - |
| EP | 293 | 351 | 58 | 328 | - |
| BOZ-EP | 128 | 256 | 128 | 211 | 244 |
| BOZ-EP with 1wt Nanene-001 | 126 | 254 | 128 | 220 | 248 |
| BOZ-EP with 1wt% Nanene-001 | 127 | 260 | 133 | 221 | 252 |
| BOZ-EP with 0.7wt% Nanene-002 0.3wt%Nanene-001 | 134 | 255 | 121 | 215 | 247 |

Figure 3 shows the DSC thermographs of the neat BOZ-EP resin, and the nanocomposites with the single Nanene-001 and Nanene-002 and 1wt% or 0.7wt% Nanene-002 + 0.3wt% Nanene-001. The neat BOZ-EP shows a sharp endothermic peak at 274ᵒC and is probably due to decomposition of part of the copolymer structure. The addition of both graphene powders as single fillers or mixed filler blend delays the curing reaction (22). This delay is less evident in the mixed Nanene-001: Nanene-002 blend than nanocomposites with a single filler content (Figure 3). The BOZ-EP with single Nanene-001 or Nanene-002 filler showed the curing exothermic peak shifted to relatively higher temperature of 10ᵒC and 9ᵒC respectively, (Table 1) compared to the neat resins. The smallest shift of 4ᵒC was observed in the mixed Nanene-001 and Nanene-002 filler, which could be attributed to a better-quality dispersion (Figure 8b) within the copolymer matrix due the different lateral sizes of the graphene flakes. This is supported by SEM imaging showing a high-quality uniform dispersion of the mixed blend nanofiller within the copolymer matrix, and by the measured mechanical properties. Additionally, curing of this system was seen to take place over the shortest temperature range of 121ᵒC, significantly shorter compared to the neat copolymer and single filler systems, (Table 1) further demonstrating the positive effect of the mixed Nanene-001 and Nanene-002 fillers.



**Figure 3.** Non-isothermal DSC of the BOZ-EP resin and nanocomposites with single Nanene-001, Nanene-002 and 0.7wt% Nanene-002+ 0.3wt% Nanene-001; at a heating rate of 2ᵒC/min, under N₂ flow, showing exothermic peaks of the curing reaction.

The total curing enthalpy *ΔHTotal* (J/g) values of all studied samples were calculated through non-isothermal DSC runs at a heating rate of 2ᵒC/min for the individual BOZ and EP systems (Figure 2) in addition to the developed neat BOZ-EP, and the nanocomposite with 0.7wt% Nanene-002 and 0.3wt% Nanene-001, (Table 2). The *ΔHTotal*(J/g) was determined for the neat BOZ-EP resin and composite with nanofillers by deconvolution and integration of the peak-1 and peak-2 correspondingly. A reduction in *ΔHTotal* of 2.5% was measured in the BOZ-EP with 0.7wt% Nanene-002 + 0.3wt% Nanene-001 vs neat BOZ-EP (Table 2).

**Table 2.** Exothermic heat of curing (ΔΗTotal) for the individual systems, copolymer, and copolymer with 0.7wt% Nanene-002 + 0.3wt% Nanene-001 obtained under non-isothermal conditions at a heating rate of 2ᵒC/min

|  |  |
| --- | --- |
| **BOZ, EP, BOZ-EP resins, and Nanocomposites** | ***ΔH Total* (J/g)** |
| BOZ | 342.8 |
| EP | 94.6 |
| BOZ-EP 1:1 wt/wt | 379.3 |
| BOZ-EP with 0.7wt% Nanene-002 0.3wt% Nanene-001 | 370 |
| BOZ-EP with 1wt% Nanene-002 | 261.3 |
| BOZ-EP with 1wt% Nanene-001 | 238.4 |

**3.2** **Curing investigation by isothermal DSC**

Isothermal DSC at 180ᵒC and 200ᵒC each for a 2 h period, (Figure 5a) were run to replicate the used curing schedule followed by the cooling back to RT of the neat copolymer and a dynamic run at 10ᵒC/min to check for any residual cure peak. To confirm the complete curing of the material a standard dynamic run at a heating rate of 10ᵒC/min was compared with the dynamic run at 10ᵒC/min, (Figure 5b) following the 2 isothermal DSC runs. The absence of any residual cure peak verifies the complete curing of the material using the stated curing schedule.

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| **Figure 4.** (a) A two-stage replication of the curing schedule used; 2h at 180ᵒC followed by 2h at 200ᵒC (b) Comparison of a dynamic DSC recorded after the isothermal runs and comparison with a dynamic obtained from an uncured sample both at a heating rate 10ᵒC/min, under N₂ flow. | |

**3.3** **Thermogravimetric Analysis (TGA)**

TGA curves for the neat PBOZ, neat PBOZ-EP copolymer, copolymer with single Nanene-001 filler and 0.7wt% Nanene-002+ 0.3wt% Nanene-001 mixed nanofillers are presented in Figure 5.

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**Figure 5.** TGA curves obtained from neat PBOZ, PBOZ-EP 1:1 wt/wt and nanocomposite systems with a mixed blend filler 0.7wt% Nanene-002 + 0.3wt% Nanene-001 and a single filler at 1wt% Nanene-001 at a heating rate of 10C/min, under N₂ flow.

At a 5% weight loss the corresponding initial decomposition temperature (Tinit) was observed to increase by 14ᵒC from 311ᵒC for the neat PBOZ to a maximum 325ᵒC for the single Nanene nanofiller system (Table 3). The neat PBOZ-EP and 0.7wt% Nanene-002 0.3wt% Nanene-001 mixed nanofiller systems also showed an improvement of 10ᵒC and 9ᵒC respectively. This improvement in thermal stability can be observed to extend to 10% weight loss for all systems to a maximum 341ᵒC compared to 332ᵒC for the neat PBOZ (Figure 5). At 50% weight loss the thermal stability of all systems drops by a maximum temperature of 31ᵒC compared to 460ᵒC for the neat PBOZ system (Table 3), (Figure 5).

**Table 3**. Characteristic temperatures of degradation

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **PBOZ-EP and Nanocomposites** | **Tonset (°C)** | **Tend (°C)** | **Te-To**  **(°C)** | **T5% (°C)** | | **T10% (°C)** | | **T50% (°C)** | |
| PBOZ | 300 | 489 | 189 | | 311 | | 332 | | 460 | |
| PBOZ-EP | 317 | 514 | 197 | | 321 | | 339 | | 438 | |
| PBOZ-EP 0.7wt% Nanene-002 + 0.3wt% Nanene-001 | 320 | 510 | 190 | | 320 | | 340 | | 429 | |
| PBOZ-EP 1wt% Nanene-001 | 322 | 517 | 195 | | 325 | | 341 | | 430 | |

## 

## **3.4 Mechanical properties**

PBOZ-EP tensile samples were produced, and the results obtained from mechanical testing formed baseline values for the different nanocomposite systems. Nanene-001 filler showed the highest decrease in E of 21% (Figure 6a). An increase in TS was measured in both single Nanene-001 and Nanene-002 nanofiller systems (Figure 6b) with a respective 27% and 21% improvement with the single Nanene measuring the most significant increase in EB (Figure 6c) of 45%. This demonstrates a good uniform dispersion of the smaller lateral size filler at this specific loading produces a material with superior strength and elastic properties compared to the neat copolymer system.

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| **(c)** | |
| **Figure 6. (a)** Tensile modulus **(b)** Tensile Strength **(c)** Elongation at break | |

Copolymers of BOZ and EP resins (1:1 wt/wt) showed a 18% and 30% drop in the TS compared to the respective single BOZ and EP resin systems, values obtained from the technical datasheets provided. The loss in tensile strength through copolymerisation was recovered and increased by 35% in addition to a 36% increase in the EB using the best 0.7wt% Nanene-002 + 0.3wt% Nanene-001 mixed lateral size nanofillers whilst the E showed a negligible 1.6% reduction. Such a negligible change in E (Figure 6a) with significant improvements in strength (Figure 6b) and EB (Figure 6c) are attributed to the uniform dispersion of the mixed graphene powders and strong interactions and stress distribution between the mixed graphene powders and copolymer matrix.

The mechanical properties comparison of the above two systems with mixed blend nanofillers demonstrates not only the positive influence of graphene in the copolymer matrix with respect to TS and EB but the possibilities for further material optimisation with the introduction of a specific ratio mixed lateral size nanofillers.

Similar reductions in E and strength was reported by (43) using a PBOZ-CER (cycloaliphatic epoxy) copolymer. Additionally, an increase in TS of 20% and 37% respectively from the base copolymer system was reported using a 1.8wt% and 0.9wt% GNPs dispersed via ultrasonication and three-roll milling. Furthermore, a significant increase in the E of 46% and 55% was observed at the above loadings and related dispersion methods. However, this increase in E also saw a reduction in the EB at all Nanene-002 loadings (43). This is in contrast to the current work, which showed the above stated improvements in strength and EB, with a negligible change in the E.

# **3.5 SEM Analysis**

The cryogenic fracture surfaces of the neat PBOZ-EP copolymer and mixed blend nanofillers were evaluated by SEM to assess the quality of dispersion within the copolymer matrix.SEM images of PBOZ-EP, PBOZ-EP 0.7wt% Nanene-002 + 0.3wt% Nanene-001 and PBOZ-EP 0.7wt% Nanene-001 + 0.3wt% Nanene-002 are presented in Figures 7a to 7c. Figure 7a shows the neat PBOZ-EP copolymer fracture surface morphology with a smooth surface showing minimum deformation, characteristic of brittle materials (27), (37). PBOZ-EP with 0.7wt% Nanene-002 + 0.3wt% Nanene-001 (Figure 7b) shows an even uniform distribution with random orientation of the Nanene-002 and Nanene-001 in the best performing mixed nanofiller blend with the highest TS. A similar uniform dispersion was reported in a PBOZ-Nanene-002 system by (37).

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| **(c)** | |

**Figure 7.** SEM micrographs obtained from (a) PBOZ-EP (b) PBOZ-EP 0.7wt% Nanene-002 + 0.3wt% Nanene-001 (c) PBOZ-EP 0.7wt% Nanene-001 + 0.3wt% Nanene-002.

In contrast to this is the poor homogeneity of the worst performing 0.7wt% Nanene-001 + 0.3wt% Nanene-002 mixed nanofiller (Figure 7c) where multiple large agglomerates of Nanene-001 and Nanene-002 can be observed, (43). The large agglomerates in the current work are a result of the incorrect ratio of the different lateral size nanofillers and the way they interact during ultrasonication in solvent and subsequent blending with the PBOZ-EP copolymer leaving areas of material predominantly made up of the matrix which is evident by the fracture surface.

# **4. Conclusions**

In the current work, five series of novel PBOZ-EP copolymer and nanocomposites were prepared, comprising of the neat copolymer, two single filler and two mixed filler blends. It was found that pre-dispersion of the graphene powders in toluene significantly improves the quality of dispersion, confirmed by SEM imaging, within the copolymer. It was shown by DSC that the addition of either single filler caused a delay in polymerisation and an increase in exothermic peaks temperature of the curing reaction with a related reduction in Δ*H*Total. compared to the neat copolymer*.* The delay in polymerisation, increased shift in exothermic peak temperature and reduction in (Δ*H*Total.) for the 0.7wt% Nanene-002 0.3wt% Nanene-001 mixed nanofiller blend were less in comparison. Additionally, through TGA it was shown that copolymerisation and the addition of graphene improved the thermal stability of the material through the range of 300ᵒC – 350ᵒC compared to the neat PBOZ system. The PBOZ-EP-0.7wt% Nanene-002 + 0.3wt% Nanene-001 samples measured the highest improvement in TS, a negligible reduction in E and a significant increase in EB. The single nanofiller systems also measured increased TS and EB demonstrating the positive effect of the graphene powders as a reinforcement. The improvements in TS and the substantial increase in elastic properties through the addition of graphene powders demonstrate these nanocomposites to be viable materials for manufacturing.

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**Conflicts of Interest:** The authors declare no conflicts of interest.

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