Affiliation:

¹Department of Metallurgical &

Materials Engineering, Indian Institute of Technology Roorkee,

^{2(present address)} Applied Science

Cluster, School of Advanced Engineering, UPES, Dehradun

248007, Uttarakhand, India.

goyatmanjeetsingh@gmail.com

Roorkee 247667, India.

Correspondence:

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Influence of ZrO₂ nanoparticles on T_g and thermal stability of epoxy

M.S. Goyat^{1,2}

ABSTRACT

 ZrO_2 nanoparticles were loaded from 0.5 to 20 wt% into epoxy using an optimized ultrasonic dual-mixing procedure to investigate their influence on glass transition temperature (Tg), thermal stability. Tg and thermal stability of the nanocomposites were examined in relation to the size of nanoparticle clusters and interparticle spacing. Nanoparticle dispersion in epoxy was characterized using atomic force microscopy. Thermogravimetric analysis was utilized to investigate the thermal stability of the nanocomposites, while differential thermal analysis was employed to estimate Tg. It was discovered that a key threshold of approximately 5 wt% for significant increases in Tg and thermal stability is reached at this nanoparticle content. The reason for these improvements is that the uniform dispersion of the nanoparticles forces the establishment of a strong epoxy-nanoparticle interface, which limits the mobility of the epoxy polymer chains. Moreover, heat transfer through the matrix is restricted by the zirconia nanoparticles, which serve as thermal insulators.

KEYWORDS: Epoxy; ZrO₂; T_g; Dispersion; Thermal stability.

1. Introduction

The adhesive and coating industries, the sports sector (for making helmets, skis, sticks and rackets), the aerospace industry, and the automotive industry are just a few of the many uses for cross-linked thermoset epoxide group-based polymers [1–5]. This wide range of applications results from

the remarkable performance of cross-linked polymers (epoxy) under various stresses. Epoxy, for instance, offers exceptional mechanical and physical qualities, low shrinkage, and high resilience to heat and chemicals [1–5]. Nevertheless, a strongly cross-linked network gives epoxy a brittle nature,

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indicating inadequate resistance to stop cracks from spreading and leading in low toughness in the finished product's use. A wide range of nanofillers have been explored, including graphenes [6–8], MXenes [9,10], spherical nanoparticles [11–14], carbon nanotubes [15] and nanoclays [16,17]. The shapes, sorts, and characteristics of these nanofillers vary greatly. Due to their wide aspect ratio, one- and two-dimensional materials including graphene, carbon nanotubes, and MXene have gained popularity as fillers for various polymers [2,9,18–20]. Yet, due to their high conductivity, these materials cannot be utilized in applications that need electrical insulation. Plus, it's hard to evenly disperse these high aspect ratio nanoparticles in viscous polymers like epoxy. Moreover, the method becomes more complex and expensive when functional materials are required, which makes it difficult to apply on an industrial scale. The fact that these materials are naturally hazardous is a serious issue that restricts their application in numerous industries. But these issues are basically non-existent when it comes to ceramic nanoparticles like zirconia, titania, alumina, etc. Because of their aspect ratio (\sim 1), these nanoparticles are readily available, affordable, and easier for dispersion in viscous polymers [21–23]. Nonetheless, ZrO₂ nanoparticles are acknowledged as the best material to use for strengthening epoxy-like polymers [24–29]. Agglomeration between nanoparticles is frequently caused by strong van der Waals forces. The most efficient technique for guaranteeing uniform dispersion of nanoparticles in viscous polymers such as epoxy is ultrasonic dual mixing [30]. ZrO₂ nanofillers are added to epoxy nanocomposites to improve their thermal stability and glass transition temperature (Tg) [31,32]. Nonetheless, no systematic investigation has been carried out to date to assess the thermal stability of epoxy-ZrO₂ nanocomposites.

For assessing thermal stability of epoxy-ZrO₂ nanocomposites, a comprehensive investigation encompassing a broad range of nanoparticle loading into epoxy, from 0.5 wt% to 20 wt%, is carried out. Zirconia nanoparticles are uniformly distributed in epoxy using UDM.

2. Experimental

Two components of the Loctite E60-HP glue were obtained from Loctite Hysol in the USA. The epoxy resin was made from diglycidyl ether of bisphenol-A, while the hardener was created from aliphatic polyamine. Sigma Aldrich in India provided the methyl ethyl ketone (MEK). American Elements, USA, provided the ZrO₂ nanoparticles, which had an average size of roughly 25 nm.

Utilizing an optimized ultrasonic dual mixing (UDM) [22], epoxy-ZrO₂ nanocomposites with 0.5–20 weight percent nanoparticles were prepared. A different study [22] reports on the UDM process [33] and its optimized components. MEK was added to the mixture during UDM processing. MEK was extracted from the mixture by evaporation at 70 °C under high vacuum following UDM processing [33]. In compliance with the material supplier's technical facts sheet, an aliphatic polyamine-based curing agent (or hardener) was blended with the epoxy resin nanoparticles. Then the resulting mixture was blended by utilizing an impeller at a very low speed of 300 rpm for 10 min and the trapped air was extracted under intense vacuum. The final step involved pouring the material into a Teflon-covered petri dish and letting it cure for a full day at room temperature. Before being described, the cured substance was removed from the petri dish and cleaned with acetone.

Using a Bruker D8 Advance Diffractometer operating at 40 kV and 40 mA, under 1.54 Å Cu-Kα radiation, phase identification of zirconia nanopowder and epoxy nanocomposites was achieved. Every step was dwelled in for 2 s. Before being analyzed, the nanocomposites were ground into a fine powder. Using Fourier transform infrared (FTIR) spectroscopy, the molecular structural characteristics of the specimens were described. Specimens were originally ground into a fine powder. After that the powder was combined with potassium bromide (KBr, Aldrich, 99.9%) and made into a transparent film for infrared analysis by pressing it through a die with a 10-ton load. Using a Thermo Nicolet Nexus 1600 FTIR spectrometer, the infrared spectra were captured under ambient circumstances. AFM (NT-MDT, Ntegra) and tapping mode atomic force microscopy were used to study the morphology of cured epoxy nanocomposites. Using AFM pictures of the nanocomposites and ImageJ software to analyze the images, the distribution of nanoparticles and their cluster sizes in the epoxy matrix were determined [18]. By employing a differential thermal analyzer (DTA) and thermogravimetric analyzer (TGA) (Perkin Elmer, Pyris Diamond), the nanocomposites from the bulk samples were broken down into tiny pieces of around 3 mm for characterization. Each specimen, weighing about 20 mg, the rate of heating was 10 °C per min between 30 and 700 °C using a N₂ purging gas flow rate of 200 ml/min. According to the DTA analysis, the glass transition temperature (Tg) was determined in accordance with ASTM E1356 standard [18], and thermal stability was estimated using TGA thermograms. The DTA measurements were conducted using a N₂ purging gas with a heating rate of 10 °C/min within an operational temperature range of 30–300 °C. In order to display the mean values along with the standard deviation, at least three repetition tests were carried out for each composition. The reference material for the thermal measurements was a 20 mg weight sample of extremely pure alumina powder.

3. Results and Discussion

3.1. Structural analysis

XRD pattern of ZrO₂ nanoparticles is displayed in **Fig. 1**. The monoclinic phase was indicated by the zirconia

nanoparticles high diffraction peaks at 28° and 31°. Every peak matches the conventional spectrum quite well (JCPDS No.: 37-1484). The XRD pattern of epoxy-ZrO₂ nanocomposites is depicted in Fig. 2. The XRD pattern for very low nanoparticle content (0.5 wt%) in the resulting epoxy-ZrO₂ nanocomposites shows practically no detectable crystalline peaks due to very low content which is insufficient to get a detectable signature in the record. That might be the reason that ZrO₂-epoxy nanocomposites show several crystalline peaks only for nanoparticle content of 1 to 20 wt%. When ZrO₂ nanoparticles are added to epoxy adhesive, the broad hump of neat epoxy becomes much less intense. As the number of nanoparticles increases, the intensity of the broad hump of neat epoxy decreases because the crystalline peaks of ZrO2 nanoparticles and the broad hump of neat epoxy have very different intensities. All the peaks in the ZrO₂-epoxy nanocomposites are exactly at same locations as the position of peaks observed in case of ZrO₂ nanoparticles Therefore, there is no structural alteration or new phase formation in the base matrix when ZrO₂ nanoparticles are incorporated into epoxy via the UDM approach.



Fig. 1. XRD pattern of ZrO₂ nanoparticles.

The FTIR spectrum of ZrO₂ nanoparticles (**Fig. 3**) shows a broad band centered at 3429 cm⁻¹ corresponds to the OH bond stretching as well as deformation due to the absorption of molecular water and coordination water, respectively [34]. The peaks centered at 1629 cm⁻¹ attributes to the OH group, which is free H₂O related to alcohol and hard to avoid in processing in ambient condition [35]. The peak centered at 1381 cm⁻¹ is corresponding to the bond of metal and hydroxide (i.e. Zr-OH group) [35]. Peak centered at 749 cm⁻¹ corresponds to the bond of metal and oxygen (i.e. Zr-O bond) of the ZrO₂ nanoparticle [36], whereas low intensity peak

centered at 450 cm⁻¹ indicates the bond of metal, oxygen and metal (i.e. Zr–O–Zr bond) [37]. The peak that is observed centered at 1019 cm⁻¹ is attributed to the stretching of Zr-O bond in bond of metal and hydroxide, Zr-OH group; presence of this band indicates the presence of hydroxyl group onto the surface of the nanoparticle, which would result in more difficulties in breaking clusters of nanoparticles.



Fig. 2. XRD pattern of epoxy- ZrO₂ nanocomposites.

Fig. 4 displays the FTIR spectra of epoxy-ZrO₂ nanocomposites. The assignment of the main transmittance bands in the FTIR spectra of neat epoxy [38–40] are indicated by alphabets 'A' to 'P' which are indicating the bands at 3418, 3060, 2924, 2360, 1727, 1608, 1510, 1461, 1360, 1290, 1250, 1182, 1107, 1036, 828, 730 and 698 cm⁻¹, respectively. The O-H stretching of the hydroxyl group is responsible for these bands, C-H vibration of epoxy ring, CH₃ methyl group vibration, atmospheric CO₂ vibration, aromatic C=O stretching, aromatic C=C stretching, aromatic ring stretching, CH₃ asymmetrical bending, CH₃ symmetrical bending, epoxy ring mode: the C-C, C-O and C-O bonds all stretching in phase, CO vibration of the epoxy ring, C-N stretching, C-O-C stretching, aromatic C–O stretching, aromatic ring bent out of plane and doublet due to aromatic ring vibration, respectively. When 0.5 to 20 weight percent ZrO₂ nanoparticles are added to epoxy, no additional peaks appear in comparison to the clean epoxy. Which indicates no new chemical bond formation takes because zirconia nanoparticles were added to the epoxy. However, O-H stretching band shows almost negligible shifting in the spectra of epoxy-ZrO₂ nanocomposites due to presence of very small amount of hydroxyl group on the surface of ZrO₂ nanoparticles. Accordingly, it appears that the amount of hydroxyl group on the surface of the nanoparticles determines how much the epoxy matrix's hydroxyl group may stretch. Additionally, high loading of nanoparticles does

not disturb the chemical structure of epoxy as revealed by FTIR spectra of epoxy-ZrO₂ nanocomposites.



Fig. 3. FTIR spectra of ZrO₂ nanoparticles.



Fig. 4. FTIR spectra of epoxy-ZrO₂ nanocomposites.

3.2. Morphology of epoxy-ZrO₂ nanocomposites

Fig. 5 shows AFM images of epoxy-ZrO₂ nanocomposites with nanoparticle contents of 3, 5, 10, and 20 wt%. The clustered nanoparticles are indicated by dotted circles and individual nanoparticles are designated by the solid circles. Majority of the nanoparticles are homogeneously dispersed

for the nanocomposite containing 3 wt% and 5 wt% nanoparticle with nominal clustering (**Fig. 5a and 5b**). While for the nanocomposite containing 10 wt% and 20 wt% nanoparticle content, only limited particles are appearing as individual particles whereas most of the particles are in clustered form (**Fig. 5c and 5d**). Thus, for ZrO₂ nanoparticles (~ 25 nm), the effective dispersion threshold for nanoparticles in epoxy is 5 wt%. This suggests that enough energy is produced by the improved UDM to allow the nanoparticles to disperse into the epoxy to their individual level. However, beyond this limit, UDM is not effective to break the cluster of particles up to individual level into epoxy. For a high particle content up to 20 wt% to be successfully dispersed, additional process parameter optimization of the UDM technology is necessary.





concentration nanoparticles The of versus average cluster size is shown in **Fig 6**. When epoxy encompasses nanoparticles at concentrations between 0.5 to 5 wt%, there is a slight increase in cluster size equivalent to \sim 2 times rise in the cluster size. However, with the further increase in the concentration of nanoparticles up to 20 wt%, the cluster's size grows almost linearly up to 133 nm. Based on both theoretical calculations and experimental data, Fig. 7 shows the nanoparticle concentration vs average interparticle distance. The theoretical inter-particle distance was calculated using a theoretical equation based on cubic distribution of particles in a polymer [41].



Fig. 6. Nanoparticle content versus average cluster size of epoxy-ZrO₂ nanocomposites.



Fig. 7. Nanoparticle content versus average interparticle distance of epoxy-ZrO₂ nanocomposites.

The detail about the theoretical equation is available in earlier published work [42]. The theoretical value for inter-particle distance is marginally smaller than the one that is measured experimentally due to presence of some form of clusters of nanoparticles for every concentration. It is clear that when the concentration of nanoparticles in epoxy rises, the space between particles decreases. The experimental and theoretical average inter-particle distance for threshold limit of nanoparticle (5 wt%) dispersion into epoxy are ~ 95 nm and ~ 82 nm respectively, which can limit the polymer chain's mobility effectively and can significantly affect the thermal properties of the nanocomposites.

3.2. Tg of epoxy-ZrO₂ nanocomposites

Fig. 8 displays the Tg of epoxy-ZrO2 nanocomposites for increasing the nanoparticle loading from 0.5 to 20 weight percent using DTA curves. In Fig. 9, the Tg trend (together with the standard deviation) is displayed. From 0.5 to 5 weight percent, the Tg of the nanocomposite increases steadily as the nanoparticle content rises; however, after this point, the T_g value monotonically decreases up to 20 weight percent of particle content. When compared to neat epoxy, the epoxy-ZrO₂ nanocomposite's Tg can rise by up to 29% at a threshold limit of 5 weight percent particle loading. The effect of cluster size on Tg of the epoxy-ZrO₂ nanocomposites is shown in Fig. 10. It is observed that the Tg of the nanocomposite goes on increasing with the increase in the size of the clusters from 30 to 58 nm but beyond this limit a decline in the Tg has been observed for increasing cluster size from 72 to 133 nm. However, a second order polynomial relation is found as $T_g = -0.004 x^2 + 0.542 x + 64.264$ with correlation factor, $R^2 = 0.587$, indicating a good relation between T_g and cluster size. Additionally, it has been observed that the behaviour of the Tg of the epoxy-ZrO₂ nanocomposites depend on the nanoparticle content and on the cluster size. Therefore, when the nanoparticle loading is increased to 5 wt% with a cluster size of 58 nm (containing about two nanoparticles), the Tg of the epoxy-ZrO2 nanocomposite is significantly higher than that of the neat epoxy. However, if the nanoparticle content is increased further to 20 weight percent with a cluster size of 133 nm (containing approximately 5 nanoparticles), the nanocomposite's T_g is significantly reduced.

The rise in Tg indicates that the influence of matrix/particle interfacial interactions must restrict the polymer chains [43]. Therefore, the presence of particles strengthens the action of cross-linking and limits the mobility of the polymer chain. By raising the apparent crosslink density, zirconia nanoparticles can function as physical crosslinkers [44]. One possible explanation for the rise in T_g is the significant amount of immobilized polymer that forms at the interface between epoxy and well-dispersed ZrO₂ [44]. It is anticipated that the increase in T_g will be proportional to the nanoparticle's surface area; thus, only when the particles are evenly distributed throughout the base matrix should the T_g rise as the nanoparticle concentration does. With a nominal clustering of around two nanoparticles, practically individual nanoparticles are uniformly dispersed in the base matrix of epoxy-ZrO2 nanocomposites (having 5 weight percent of nanoparticle content). But the rise in nanoparticle content beyond 5 wt% to 20 wt% results in significant increase in the

cluster size from 86 to 133 nm (containing \sim 3 to 5 nanoparticles) that may decrease the extent of cross-linking and therefore resulting the decrease in the T_g. Therefore, the ZrO₂ nanoparticles are prone to clustering because of their very high specific surface area and dominance of strong Van der Wall forces due to their nano size. That makes the breaking of clusters difficult and thereby restricts their advantage regarding improving the Tg of the resulting nanocomposite for high nanoparticle content.



Fig. 8. DTA curves representing Tg of epoxy-ZrO₂



Fig. 9. Nanoparticle content versus Tg of epoxy-ZrO2 nanocomposites.



Fig. 10. Effect of cluster size (x) on Tg of epoxy-ZrO₂ nanocomposites.

3.3. Thermal stability of epoxy-ZrO₂ nanocomposites

TGA graphs of epoxy and epoxy-ZrO₂ nanocomposites for weight losses up to 50% are shown in Fig. 11. The thermal decomposition temperature (T_d) values for nanocomposites at different weight loss percentages are displayed in Table 1.



Fig. 11. TGA curves displaying the weight remaining percentage of epoxy-ZrO₂ nanocomposites versus temperature.

Because most researchers view 50% weight loss as a sign of structural instability, this percentage of total weight loss is used in this work to determine the nanocomposites'

nanocomposites.

structural destabilization point [45]. Fig. 12 displays the variance in weight loss percentage versus Td for neat epoxy and epoxy-ZrO2 nanocomposites. The Td of the epoxy nanocomposite, which contains 5 weight percent ZrO₂ nanoparticles, is determined to be 346 °C for a 10% weight loss, while the neat epoxy's T_d is 307 °C for the same percentage of weight loss. The T_d of the neat epoxy at 50% weight loss of the material is found to be 375 °C, while the Td of the epoxy nanocomposite (which includes 5 wt% ZrO₂ nanoparticles) is 407 °C. Consequently, the thermal stability of epoxy nanocomposite is higher than that of neat epoxy as the concentration of nanoparticles rises from 0.5 to 5 wt%. However, a significant drop in the thermal stability of the nanocomposite occurs when the loading of nanoparticles in epoxy is increased to 20 wt%. Table 1 shows that at 700 °C, the neat epoxy's TGA curve produced a char yield percentage of around 9.75. The TGA curves of epoxy nanocomposites with 20 wt% of particles indicate that 17.29 is the maximum char yield percent at 700 °C. Because ceramic nanoparticles (ZrO₂) are present, it is evident that as the nanoparticle concentration increases from 0.5 to 20 wt%, the char yield percentage increases monotonically.



Fig. 12. Weight loss % versus T_d of neat epoxy and epoxy-ZrO₂ nanocomposites.

Weight Remaining (%)	Thermal decomposition temperature (T _d) $^{\circ}$ C									
	Neat	Epoxy-ZrO $_2$ nanocomposites containing nanoparticle (wt%)								
	Ероху	0.5	1	2	З	5	7	10	15	20
90	307	316	322	330	333	346	338	335	332	316
80	333	339	344	351	358	361	359	353	352	345
70	347	351	356	363	371	375	372	367	366	358
50	375	378	384	392	400	407	403	396	401	389
Char yield % at 700 °C	9.75	9.95	10.78	11.52	12.23	13.51	13.95	14.41	15.83	17.67

Table 1. TGA results for epoxy-ZrO₂ nanocomposites and neat epoxy.

The degradation of the aliphatic polyamine-cured epoxy network, which serves as the base matrix in this work, must be comprehended before one can understand the degradation of epoxy nanocomposites. The breakdown process of the network of cured epoxy resin typically consists of two parts. Between 35 and 310 °C, the first stage is brought on by the evaporation of leftover solvent and adsorbed humidity. [46]. The heat breakdown of the cured epoxy network causes the second step to occur between 310 and 450 °C. Dehydration leads to the aliphatic polyamine-cured epoxy network's degradation because it removes water molecules from the oxypropylene group (-CH₂-CH(OH)-). This happens while the epoxy network breaks down and

double bonds are formed [46]. Additionally, the (O-CH₂) and (CH-CH₂) bond scission processes run concurrently. Unsaturated phenolic compounds are the result of the degradation and are either emitted as gaseous products or polymerize to produce char [46].

TGA thermograms (**Fig. 11**) thus show that the degradation of epoxy nanocomposites likewise follows a twostage process. Since ZrO₂ nanoparticles are ceramic, they prevent heat from passing through the epoxy when they dispersed evenly [45,47,48]. Because more nanoparticles form more obstacles. Thus, the resulting nanocomposites' capacity to endure heat is enhanced. But when the content of the particles increased up to 5 wt%, the particle-to-polymer interface becomes more dominant than the particle-toparticle interface, which leads to increased thermal stability. However, further increase in particle concentration results in a noticeable clustering which reduces the cross-linking density. Because of their often-high cross-linking density, thermosetting polymers have high breakdown temperatures [49]. The cross-linking density is greatest when the entire stoichiometry of the epoxy matrix is maintained. The stoichiometry of the epoxy matrix will fail if foreign particles (ZrO₂) are added over a certain limit [49]. This will drop the decomposition temperature and diminish the crosslink density. Therefore, a decrease in the decomposition temperature is observed when the nanoparticle content surpasses the threshold limit. Epoxy nanocomposites with nanoparticle quantities over their threshold limit (5 wt%) show less heat retardant action, leading to decreased thermal stability, because of the clustering of particles.

3.4. Thermal degradation kinetics of epoxy-ZrO₂ nanocomposites

The kinetic analysis provides information about the mechanism of polymer breakdown together with indications about the energy barriers of the process. The well-known Coats Redfern model (CR) [50] and integral model of Horowitz and Metzger (HM) [51] have been employed in this work to collect kinetic data on the thermal degradation of epoxy composites. **Fig. 13** shows the CR plots of epoxy nanocomposite and epoxy treated with one order reaction. **Fig. 14** shows the Horowitz and Metzger plots of neat epoxy and epoxy composite.



Fig. 13. The Coats Redfern method-based heat degradation kinetics of neat epoxy and epoxy-ZrO₂ (3%) nanocomposite.

Fig. 15 shows the (activation energy) E_a of neat epoxy and epoxy composites, which were calculated using HM and CR plots. For epoxy-ZrO_2 nanocomposites, both the CR and HM techniques show that the activation energy of

decomposition rises as the nanoparticle content increases from 0.5 to 5 wt% and falls as the nanoparticle content increases up to 20 weight percent (**Fig. 15**). The activation energy determined using CR method reaches a maximum value of ~ 122 kJ/mol for 5 wt% epoxy-ZrO₂ nanocomposite. But the activation energy calculated using HM method for the same nanocomposite reaches a maximum value of ~ 135 kJ/mol. Therefore, the addition of ZrO₂ nanoparticles to epoxy leads to a significant increase in the resulting nanocomposite's E_a of decomposition, which bears responsibility for the increased thermal stability of the nanocomposite.



Fig. 14. Horowitz–Metzger method-based heat degradation kinetics of neat epoxy and epoxy-ZrO₂ (5%) nanocomposite.



Fig. 15. CR and HM methods-based $E_{\rm a}$ of decomposition of the neat epoxy and epoxy-ZrO_2 nanocomposites.

For epoxy nanocomposites, ease of decomposition likewise exhibits a pattern like thermal stability. When comparing the epoxy- ZrO₂ (5 weight percent) nanocomposite to neat epoxy, the greatest improvement in the E_a of decomposition is approximately 56% when using the CR method and 45% when using the HM method. Because different kinetic equations are used for HM and CR techniques of breakdown, the activation energy of decomposition for a given nanocomposite varies. The observed increment in activation energy during the decomposition of nanocomposites may be ascribed to effective structural evolution, especially when considering the distribution of homogenous nanoparticles inside the epoxy matrix. Now the elevated activation energy could potentially be attributed to the nanoparticle's ceramic nature. This is because the nanoparticles restrict the molecular motion of polymer chain segments, which enhances T_g. They can also prevent random scission epoxy network creation by restricting the heat flow in the epoxy resin. In the scenario when nanoparticles are dispersed uniformly throughout the matrix, the path of constraint to random scission of molecules is strengthened. Because there are more barriers preventing heat from passing through the matrix. When the quantity of particles in epoxy is increased beyond 5 wt%, however, the accumulation of nanoparticles and their unequal diffusion within the epoxy have a negative effect on the activation energy of breakdown, making them less effective in blocking heat.

3.5. Integral procedural decomposition temperature (IPDT)

The thermal stability of the neat epoxy and epoxy-ZrO₂ nanocomposite was further evaluated using IPDT, which is based on Doyle's method [52]. The literature contains comprehensive guidelines for calculating IPDT [53]. Using TGA thermograms, IPDT which includes the entire stability spectrum is computed in three stages: first disintegration, rapid disintegration, and the final step of char production. The IPDT of neat epoxy and epoxy composites is shown in **Fig. 16**. Using TGA curves, the IPDT for neat epoxy is calculated around 398.48 °C. But when the nanoparticle concentration rises from 0.5 to 20 wt%, the IPDT continues to rise. The largest concentration of nanoparticles (20 wt%) yields the highest IPDT value. For epoxy nanocomposite, the highest IPDT value is 535.

Due to the addition of oxide nanoparticle, the epoxy has a notably greater thermal resistance than neat epoxy. The pattern of IPDT alteration with increasing particle concentration is shown to be different from the pattern observed for E_a . According to [54], the physical differences between the IPDT and the E_a of decomposition are most likely the root reason. The specimen's overall stability is reflected by the IPDT throughout the duration of its three stages. In contrast, the E_a of decomposition only considers fast decomposition and ignores the other two components. The reason behind the rise in IPDT as particle content increases is the corresponding rise in char content. The rise in char content that corresponds with an increment in particle content is what causes the IPDT to rise.



Fig. 16. Nanoparticle content versus IPDT of epoxy-ZrO₂ nanocomposite.

4. Conclusions

ZrO₂ nanoparticles were effectively introduced into epoxy using UDM technique to develop epoxy nanocomposites. With a cluster size of 58 nm (containing \sim 2 nanoparticles) and an inter-particle spacing of around 95 nm, a threshold limit of about 5 wt% ZrO₂ nanoparticles was established. At the nanoparticle threshold limit, the T_g value greatly increased by around 29% and similarly thermal stability of the nanocomposite was prominently increased. A strong matrixparticle interaction was identified as accountable for the nanocomposite's improved T_g value and thermal stability due well-dispersed nanoparticles. It was demonstrated that the rise in T_g was caused by the chain segment mobility of the epoxy polymer lessening due to the formation of good interface the nanoparticle and polymer. The inclusion of nanoparticles restricts the free movement of polymer chains and increases the cross-linking action because they can act as physical cross-linkers by increasing the apparent crosslink density. The increase in thermal stability could be attributed to the ceramic nature of evenly distributed oxide nanoparticles, which act as insulators to the heat transfer through the polymer matrix.

Disclosure statement

The authors declare no relevant financial or non-financial interests.

Data availability

Raw data of the research article is available with the authors and will be provided as per a request from the journal.

Ethical approval

Not applicable.

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