Avani Kumar Upadhyay[1,2], *Manjeet Singh Goyat*[3, 4,*]

[1]Department of Mechanical Engineering, School of Engineering, University of Petroleum & Energy Studies, Dehradun, Uttarakhand, India, [2]CAD Department, Tendemloop Technologies Pvt. LTd., Bangalore, Karnataka, India, [3]Department of Applied Science, School of Engineering, University of Petroleum & Energy Studies, Dehradun, Uttarakhand, India, [4]Smart Materials, Mads Clausen Institute, University of Southern Denmark, Sønderborg, Denmark

Review paper
ISSN 0351-9465, E-ISSN 2466-2585
https://doi.org/10.62638/ZasMat1038

Zastita Materijala 65 (1)
126- 142 (2024

A review on improved physical and thermal properties of oxide nanoparticles reinforced epoxy composites

ABSTRACT

Epoxy resins are well-known because of their desirable thermal and mechanical characteristics in a variety of fields, including the automotive, construction, and aerospace sectors. However, the inherent brittle nature of highly cross-linked epoxy resins generally leads to weakness in resisting the formation of cracks and their movement. The brittleness of the epoxy resins is one of the major obstacles inhibiting its use at a wider scale. Therefore, many researchers focused on reinforcement of epoxy resins by different types of nanostructures including carbon nanotubes (CNTs), organic/inorganic nanofillers to provide higher strength, without diminishing other essential thermo-physical characteristics of the nanocomposites. Most of the review articles focused on the CNT-reinforced epoxy composites and very limited review articles are available that focus on the oxide nanofiller reinforced epoxy composites. In this review article, epoxy nanocomposites reinforced with alumina (Al_2O_3), titania (TiO_2), silica (SiO_2), and zirconia (ZrO_2) nanoparticles have been investigated. The influence of the oxide nanoparticles in modifying the physical and thermal properties of the epoxy nanocomposites has been presented, compared, and critically analysed to optimize the performance of epoxy nanocomposites.

Keywords: *Oxide nanofiller; glass transition temperature; physical properties; thermal properties; thermal degradation*

1. INTRODUCTION

Since the beginning of human civilization, it has been desired to combine different types of inexpensive materials to efficiently increase the performance of various types of commodity materials. Beginning with the most primitive composite material, which was composed of straw and mud, and progressing all the way up to the most cutting-edge composite materials, which are utilized in the fabrication of body components for spacecraft, several advancements in the form of the composite material have been sought for and accomplished. To make a material that has better qualities in comparison to its component materials, composites have the advantage of combining the advantageous features of their constituent materials, which is one of the benefits of using composites.

With the commercialization of polymers, numerous research interests have been drawn for the expansion of polymer-based nanocomposite because of the distinctive characteristics of these composites. These properties include low cost, good exterior, exceptional resistance to chemicals, good manufacturability, material design flexibility, large strength/weight, and balanced mechanical performance[1–3]. By selecting combinations of parts that are appropriate, it is even possible to adapt and maximize the qualities of polymer composite materials. The polymer nanocomposites have better thermal, mechanical, and electrical capabilities at low loading, and higher gas barrier qualities while maintaining clarity, improved dimensional stability, and many other desirable characteristics [4,5]. Only the well-dispersed nanofillers without significant clustering in a polymer matrix can improve the physical and mechanical properties of the resulting polymer nanocomposite up to a great extent.

One of the most known thermosetting polymers used as the base matrix to produce polymer nanocomposites is epoxy adhesive. Epoxy resins

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*Corresponding author: Manjeet Singh Goyat
E-mail: msgoyat@ddn.upes.ac.in

Paper received: 27. 09. 2023.
Paper accepted: 25. 10. 2023.
Paper is available on the website: www.idk.org.rs/journal

are having huge industrial utilization in the structural, aerospace, automotive, electronics and sportswear. Additionally due to high cross-linking capacity, epoxy composites are naturally brittle, leading to poor resistance to crack initiation and growth [6]. One of the key goals of researchers is to develop an epoxy that has a greater level of toughness, without compromising other essential features like as its thermo-physical and mechanical characteristics that are highly sought in a variety of structural applications.

To develop structural nanocomposites, many scientists investigate the reinforcement of inorganic nanoparticles apart from organic nanoparticles in the epoxy and other polymeric resins. To attain isotropic physical, thermal, and mechanical properties, nanoparticles are frequently used for reinforcing epoxy nanocomposites due to their high specific surface area and less hindrance to the cross-linking density of the epoxy resin. The cost of nanocomposites has always been a matter of great concern for few years (Fig. 1). The expensive raw materials and manufacturing processes made it difficult to use them for each automotive and aerospace application yet the mass production of the components can help in reducing the cost [7–9].

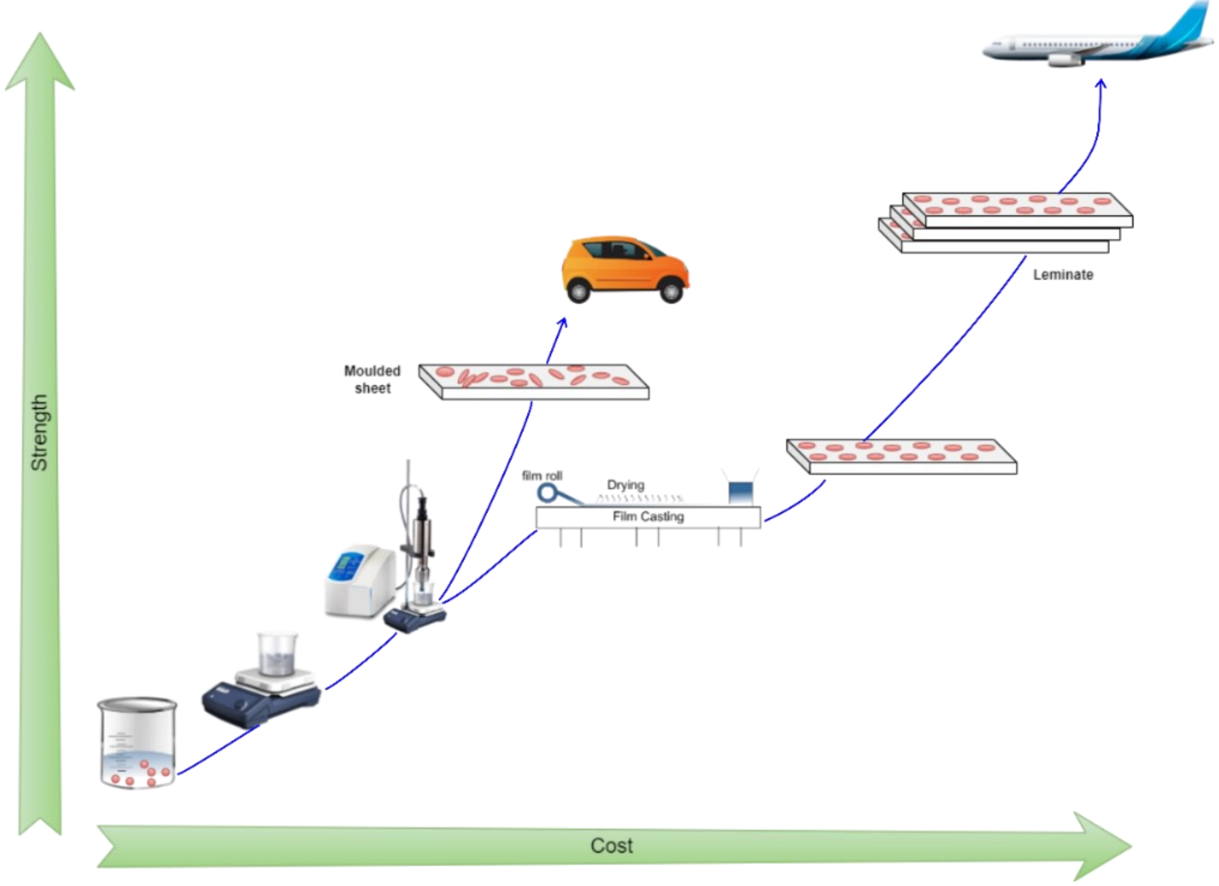

Figure 1. Relative performance and cost profiles in nanocomposite manufacturing [7]

Slika 1. Relativne performanse i profili troškova u proizvodnji nanokompozita [7]

The presence of fillers with a high specific surface area contributes to the formation of a substantial interface within the composite, assuming that the modifiers are adequately disseminated throughout the matrix. The enhancement of toughness and strength in structural ceramics and polymers has been the subject of investigation, with findings indicating considerable improvements when nanoparticles are used as building blocks, as compared to microparticles[10,11]. Furthermore, the interaction of nanoparticles and base matrix is contingent upon the surface structure, geometry, and surface chemistry of the particles, exerting a significant impact on the creation of the interface. Nanoparticles have a somewhat lower degree of matrix deformation restriction in comparison to microparticles due to their enhanced integration into the polymer microstructure, which is facilitated by their proximity to molecular dimensions. The potential impact of nanoparticles on the deformation processes of polymers at the micro or nanoscale may be anticipated based on their strong interactions with the matrix.

Extensive research has been conducted on integrating nanofillers with both low and high aspect ratios. This integration has shown promise in enhancing the toughness of polymers, as well as improving key properties like wear-resistance and electrical resistivity. Reports indicate that epoxy reinforced with Ag nanoparticles helps stabilize temperature, whereas carbon black mixed in epoxy base generates reheating properties suitable for applications involving higher voltages. Moreover, the incorporation of organoclay into epoxy results in remarkable dampness and air resistance attributes, contingent upon the specific varity of clay used [12,13]. Notably, the inclusion of aluminium hydroxide particles has been observed to enhance the flame-retardant characteristics of polyvinyl chloride. Recent research highlights the remarkable potential of hybrid fillers like $Mg(OH)_2$/lignin when added to poly(vinyl chloride) matrices. This addition significantly enhances thermal stability, demonstrating an approximate threefold increase compared to unfilled polymers [14].

In recent times, there has been a significant focus on the use of rigid spherical oxide nano-particles as fillers, as seen by the attention they have garnered in several studies[15-25]. The incorporation of stiff spherical oxide nanoparticles into epoxy glue results in a comparatively lower degree of impediment during the cross-linking process. Multiple studies have previously shown that the integration of oxide nanofiller into thermosetting plastic matrices is an efficient method for enhancing their thermo-mechanical capabilities, while still maintaining other crucial features such as T_g (glass transition temperature) and stiffness. However, the most commonly used four types of oxide nanoparticles such as Al_2O_3 [11,22,26–31], TiO_2 [20,21,25,30-42], SiO_2 [23, 31, 43–46] and ZrO_2 [15,17,47–49] are extensively utilized for reinforcing epoxy matrix to attain noteworthy alterations in its T_g, thermo-physical properties. On different occasions, the mixing of alumina nanoparticles in epoxy shows increment or decrement or no change in the T_g of the resulting nanocomposites. However, on the addition of silica nanoparticles in epoxy resin, no significant effect on T_g of the epoxy resin is reported, however, Young's modulus, fracture toughness, and fracture energy showed a noteworthy improvement [10]. This irregular pattern in T_g might be mostly due to a variety of reasons like nanoparticle size, amount, and dispersion scenario in the polymer matrix. Further, the reported studies lack a unified and systematic approach to the development of nanocomposites. Additional crucial variables like tacticity, cross-linking density and molecular weight of the nanocomposite may have a substantial influence on enhancing the material characteristics. Hence, it is important to investigate the thermo-mechanical characteristics of the epoxy matrix when supplemented with oxide nanoparticles, considering their size, quantity, and dispersion within the matrix, since these factors significantly impact the diverse toughening methods.

The full use of the distinctive influence of oxide nanofillers in enhancing the characteristics of the nanocomposite may be achieved by effective dispersion within a polymer matrix. The distribution conditions and uniform microstructure of nanofiller have a major impact on the mechanical performance. The dispersion process used for introducing nanoparticles into the polymer matrix is a crucial step in attaining the required material properties. In order to get a uniform dispersion, a range of dispersion techniques, including shear mixing [47], solution mixing [50], mechanical stirring [51] and melt mixing [52] have been utilized to incorporate nanofiller in the epoxy base. In recent years, ultrasonic cavitation has gained global recognition as a method for dispersing oxide nanoparticles in epoxy adhesives. This technique is favoured due to its convenient processing and its effectiveness in dispersing individual nanoparticles inside semi-viscous liquids[53]. The phenomenon of ultrasonic cavitation does not provide a uniform dispersion of ultrasonic energy throughout the whole of the material. Furthermore, it has been shown that the ultrasonic cavitation approach has reduced efficacy in dispersing a large concentration of nanoparticles, often above 3 wt% [33]. The challenges need the refinement and enhancement of the ultrasonic vibration procedure. Nevertheless, a recently documented pioneering method known as ultrasonic dual mixing (UDM), such as the combination of ultrasonication and mechanical mixing, presents a more favourable prospect for ensuring comprehensive contact between the entire material and the ultrasonic probe. This technique allows for a gradual exposure to ultrasonic energy, thereby maximizing its benefits while minimizing any potential degradation of the base material [22].

The primary emphasis of this article is to examine the role of oxide nanoparticles in improving the physical and thermal properties of epoxy composites.

2. POLYMER NANOCOMPOSITES

Polymer nanocomposite represent a significant class of hybrid organic/inorganic nanofiller reinforced materials containing inorganic nanofillers in shape of nanotubes, nano sheets and nanoparticles dispersed uniformly in a polymer-based matrix [54]. The variation in different physiognomies of a polymer, including crystalline structure, entanglement, mobility of polymer chain and density can considerably impact the characteristics of polymer nanocomposites even at low nanoparticle concentration compared to typical micro particles [55]. The distinctive characteristics of nanofillers are a result of their reduced size, often ranging from 1-100 nm. This reduction in size results in a substantial increase in surface area to nanoparticle volume. The dispersion state and microstructural homogeneity of nanofillers have a considerable impact on the mechanical and thermal characteristics of polymeric matrices that are reinforced with them [46].

Polymer nanocomposites are typically developed using either thermosetting or thermoplastic polymeric materials as the matrix [41,56,57]. Epoxy adhesives are the most commonly utilized thermosetting polymer because of their versatility in different industries, including the automotive, aerospace, paint and coatings, and electrical instrumentation sectors[58–60]. Epoxy adhesives are inexpensive, strong, and resistant to a wide range of chemicals and conditions. In addition, epoxy adhesives may be utilized to attach with various materials including plastic, rubber, ceramic, wood and glass, [61] etc. Epoxies have good sealing characteristics and can quickly fill gaps [62]. While epoxy adhesives do have several benefits, such as those already discussed, their brittleness prevents them from being used in complex constructions. Water absorption studies were published to evaluate the coefficient of diffusion, maximum moisture absorption, and T_g of epoxy [63], but these results do not yet provide a complete picture of the combined degradable action of moisture and temperature on epoxy. When it comes to fracture propagation resistance and hardness, epoxy adhesives fall short [30,64]. To find solutions, scientists from all around the globe have experimented with several nanofillers.

3. NANOFILLERS FOR POLYMER NANOCOMPOSITES

Numerous studies have extensively investigated polymer nanocomposites using various matrices such as polyamide-6 [65], polystyrene [66], polyetherimide [67], epoxy [68,69] along with diverse nanofillers like montmorillonite clay $CaCO_3$, TiO_2, Ag, Al_2O_3, carbon nanotubes and SiO_2 [39,46,70-73]. This study focuses on examining epoxy adhesive as the chosen polymer matrix.

Rigid spherical oxide nanoparticles as fillers have garnered huge attraction in recent studies [29,45,74]. Due to their excellent mechanical characteristics, chemical inactivity, sustainability at high temperature, and economical [15,20,22,35, 73, 75]. Oxide nanoparticles (alumina, titania, zirconia etc.) have been considered as prospective nanofillers for the industrial applications. Furthermore, because of their low aspect ratio ~1, spherical oxide nanoparticles provide less hindrance to the cross-linking of the polymer when mixed into the epoxy. Furthermore, the spherical oxide nanoparticles prevent premature failure and keep the matrix transparent. But nanoparticles attract each other due to their high surface area to volume ratio and attractive electrostatic forces (van der Waals force) resulting in agglomeration. Because the van der Waals forces become one of the strongest forces in the range of 1-10 nm. The agglomeration of nanofillers in the matrix is highly undesirable to obtain the enhancement in various properties of the developed nanocomposites [45], because, the agglomeration of nanoparticles restricts their interaction with the matrix. One of the most difficult parts of making nanoparticulate-epoxy composites with enhanced characteristics due to the challenge of homogeneous dispersion of nanoparticles in the epoxy matrix.

4. PROPERTIES OF NANOPARTICULATE-EPOXY COMPOSITES

The enhancement of properties of polymer nanocomposites can be achieved using the homogeneous dispersion of numerous types of nanoparticles in a polymer matrix. According to reports, a significant enhancement in the T_g of the bulk epoxy matrix may be attained by using a relatively small quantity of Al_2O_3, TiO_2, and SiO_2 nanoparticles [30,33,76]. However, it has been shown that the epoxy matrix supplemented with oxide nanoparticles exhibits varying behaviors in terms of increased, decreased [77], or insignificant changes in T_g [78]. Hence, it is important to acquire the knowledge about precise variation of the T_g in epoxy matrices supplemented with oxide nanoparticles. The mechanical properties of the material are also heavily influenced by the dispersion state and microstructural uniformity of the nanoparticles [46]. The integration of nanoparticles into the polymer matrix by dispersion is a crucial procedure to get the required material characteristics. The simultaneous integration of oxide nanoparticles into the epoxy matrix results in the reinforcement of epoxy matrix that can lead the enhancement of physical and mechanical properties of the matrix. The increased potential for contact between nanoparticles and the epoxy matrix is attributed to the large surface area to volume ratio [79]. The introduction of nanoparticles into the polymer matrix has the potential to impact the morphological structure of the resulting nanocomposite, hence affecting its thermo-physical, mechanical, tribological, and fracture properties [74].

Numerous parameters, including nanoparticle type, concentration, size, surface chemistry, dispersion scenario in the matrix, and immobilized particle-matrix interface, contribute to the morphological architectural shift caused by the presence of nanoparticles [79,80]. To enhance the thermo-physical characteristics of nanocomposites, a strongly immobilized particle-matrix boundary and uniformly distributed nanofiller play a primary role [81]. But a surge in nanofiller concentration in polymeric base beyond a threshold value leads to a decline in the thermo-physical characteristics due to the dominance of particle-particle interaction and thereby significant agglomeration.

4.1. Influence of Oxide Nanofiller on T_g

The oxide nanofiller such as Al_2O_3, TiO_2, ZrO_2 and SiO_2 nanoparticles are considered as prospective candidates to increase the several important characteristics of polymer nanocomposites. Many studies are reported for TiO_2 nanoparticles reinforced polymer composites to improve photocatalytic activity, thermal, viscoelastic, and mechanical properties [40,42,66,82–84]. The mixing of TiO_2 nanoparticles in the epoxy resin can increase the T_g of the resulting nanocomposite [33]. The reported enhancement in T_g for TiO_2-epoxy nanocomposites is different for a different size, content, and surface characteristics of TiO_2 nanoparticles as well as the difference in epoxy matrix properties and preparation techniques used to develop nanocomposites [30,33,38]. The reported maximum improvement in T_g for TiO_2-epoxy nanocomposite containing 1 wt% of TiO_2 nanoparticles (5 nm) is about 11 °C [33].

It is also verified that a significant enhancement in T_g can be attained by mixing low content of Al_2O_3 nanoparticles [30]. However, it has been shown that the Al_2O_3 nanoparticles reinforced epoxy exhibits inconsistent behavior, with T_g either increasing, decreasing [85], or not changing [86]. The maximum reported improvement in T_g for Al_2O_3-epoxy nanocomposite containing 5 wt% of Al_2O_3 nanoparticles (10-30 nm) is about 12 °C [87].

The ZrO_2 nanoparticles have a good capability to enhance the various characteristics of the epoxy matrix. But, the ZrO_2 nanoparticles are extensively studied for anticorrosion coatings [88-90] and wear-resistant materials [48] because of their high strength, high fracture toughness. Zirconia nanofiller work as virtuous heat resister due to their high resistivity against heat [90]. Only limited literature is available on ZrO_2 nanoparticle reinforcement. Numerous investigation have revealed that the inclusion of ZrO_2 nanofillers inside the polymer base has the potential to enhance the glass transition temperature (T_g) [47,91]. The maximum reported improvement in T_g for ZrO_2-epoxy nanocomposite containing a high content of 8 vol% of ZrO_2 nanoparticles (12 nm) is about 8 °C [47].

The observed elevation in glass transition temperature (T_g) is often ascribed to a reduction of motion of polymer chain sections inside the epoxy base, which may be related to the interaction between the matrix and nanoparticles. Only well-dispersed nanoparticles into the epoxy base can restrict the polymer chain flexibility. This is possible in two ways: (i) the generation of high interface area due to nanoparticle-matrix interaction, which can change the local dynamics of the matrix, and (ii) the very small nanoparticle surface-to-surface distance, which can limit the polymer chain segment movement. The possibility of restriction to the polymer chain segment movement is significantly increased if the nanoparticles are well dispersed in the epoxy and have a robust adhesion amongst the nanoparticles and surrounding polymer base [30]. The local fragmented mobility of matrix chain can be predicted by evaluating the fragmented relaxation period or T_g of loaded and unloaded nanocomposite. Adding oxide nanoparticles can affect the T_g of nanocomposite in three ways i.e., increase, decrease, or no change (Fig. 2). This mainly depends on the filler matrix interfacial interactions. Strong filler matrix bonding (electrostatic, covalent, H-bond) of wetted particle will leads to increase in T_g whereas large space between filler and matrix at the interface of unwetted particles is responsible for decrease in T_g [92]. Further T_g will remain unaffected due to shaky interface formation. Bansal et al. [93] studied the comparability between PNC (polymer nanocomposite) and thin polymer films. They suggested that polymer segment between two particles is analogous to a thin film of an equivalent thickness (equal to interparticle spacing).

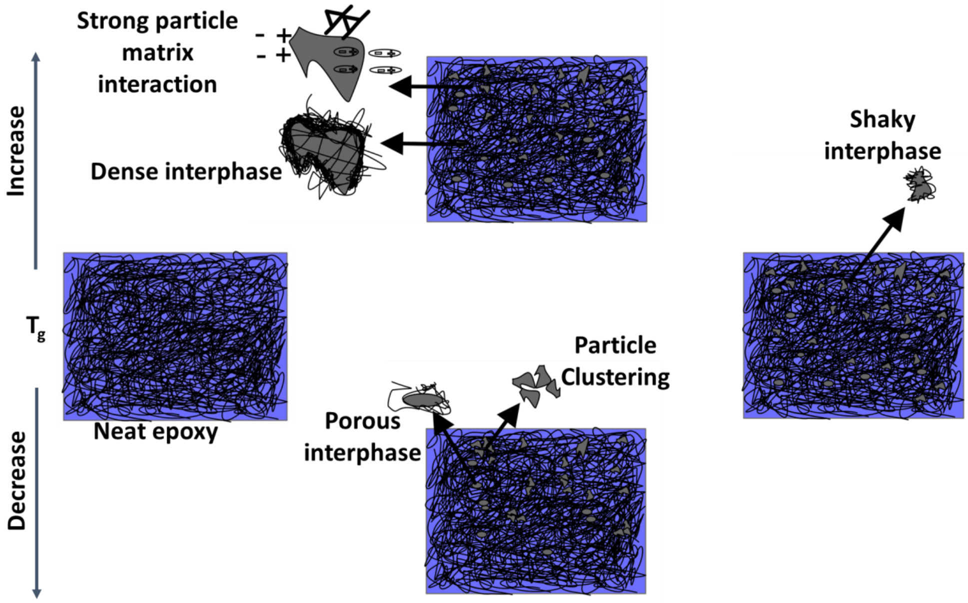

Figure 2. Schematic diagram showing mechanism of increasing, decrease and no alteration in glass transition temperature (T_g)

Slika 2. Šematski dijagram koji pokazuje mehanizam povećanja, smanjenja i bez promene temperature staklastog prelaza (T_g)

The incorporation of oxide nanoparticles in the epoxy matrix may work as extra virtual nodes for epoxy chain network, thereby resulting in the enhanced T_g [33]. Furthermore, the nanofiller may work as physical cross-linkers [30] leading to the enhanced cross-linking density of the resulting nanocomposite, and increased cross-linking density results in the enhanced T_g. Another possibility of an increase in T_g because of the development of a huge share of the restrained epoxy at the nanoparticle-matrix boundary. It is anticipated that the rise in T_g would exhibit a direct relationship with the surface area of the nanoparticle. Specifically, as the particle size decreases, the surface area increases, hence intensifying the constriction effect on the epoxy resin networks. Therefore, the restriction effect on polymer chain segment movement increases with the content along with decreasing particle size [30]. The reduction in T_g seen in systems with high nanoparticle content may be attributed to two primary factors. Firstly, the adhesion of polymer resin on the exterior of the nanofillers can cause a change in the non-stoichiometric mixture. The T_g of the epoxy-amine system is reduced due to its non-stoichiometric nature, resulting in a noticeable fall in T_g [94,95]. One potential factor is the non-uniform dispersion of nanoparticles inside the base matrix, which may be attributed to the prevalence of inter-nanofiller attraction forces [38]. This occurrence leads to particle agglomeration, resulting in a reduction in crosslinking density and subsequently a fall in the T_g.

In recent reports, an enhancement in T_g values is observed due to an increase in TiO_2 nanoparticle concentration (0.5 to 10 wt.%) in epoxy as depicted by DSC. Though at high nanofiller concentration (~20 wt%) descent in T_g values are found (Fig. 3a). 10 wt.% TiO_2-epoxy nanocomposite showed a maximum increment of ~ 27% in T_g [96]. The effect of the SiO_2 nanoparticle content on T_g is exhibited in Fig. 3b. The increased T_g values seen in SiO_2-epoxy nanocomposites fabricated using the sol-gel technique may be credited to the constrained movement of epoxy chain segments [97]. Kumar et al. [98] examined the consequence of mixing ZrO_2 nanofiller on the thermomechanical characteristics of epoxy nanocomposite. Authors revealed that increasing ZrO_2 content (up to 4 wt.%) enhances the T_g (Fig. 3c). The phenomenon described is attributed to the adhesion of epoxy atoms onto the boundary of nanofillers, resulting in a low movement of epoxy atoms. Dorigato et al. [91] investigated the improvement in epoxy adhesives with calcined zirconia nanoparticles and obtained the trends of DSC and DMTA tests of T_g for various zirconia epoxy nanocomposites. The values of T_g obtained from the peak of tan δ in dynamic mechanical thermal analysis (DMTA) testing were consistently greater compared to those obtained from differential scanning calorimetry (DSC) tests. The graph illustrates a non-monotonic trend in T_g as the zirconia concentration increases, with the greatest rise seen at a filler level of 1 vol%. The statement aligns well with the interpretations made by Dean et al. [99]. Yazman et al. [100] examined the outcomes of Al_2O_3 on the T_g of epoxy nanocomposite in his more recent study. Authors found that adding Al_2O_3 (up to 1.5 wt.%) into epoxy matrix provides around a 15% improvement in the T_g (Fig. 3d).

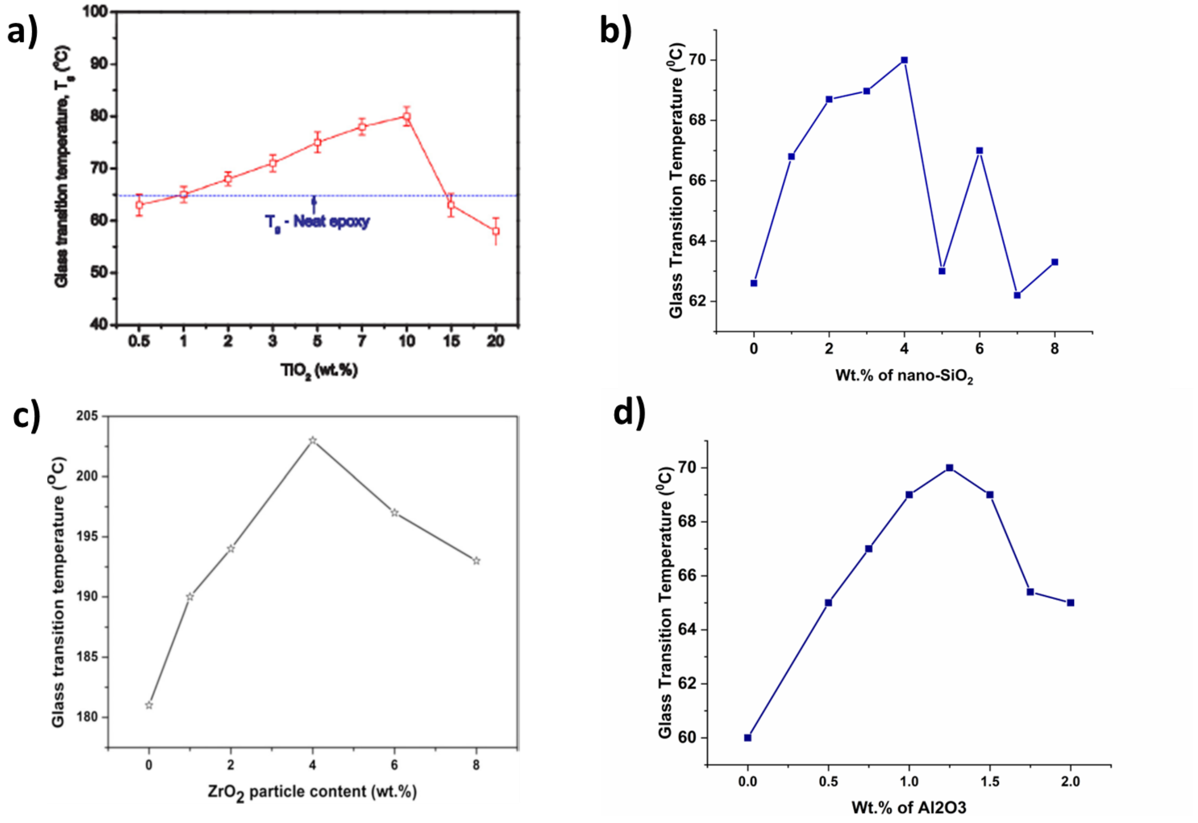

Figure 3. Variation T_g with respect to (a) wt% of TiO_2 [96] (b) wt% of SiO_2 (c) wt% of ZrO_2 [98] (d) wt% of Al_2O_3

Slika 3. Varijacija T_g u odnosu na (a) tež.% TiO_2 [96] (b) tež.% SiO_2 (c) tež.% ZrO_2 [98] (d) tež.% Al_2O_3

Reduced epoxy chain segment movement, high cross-linking density, and dense interphase formation were the reported reasons for the same. The observed drop in T_g with increasing filler amounts may be attributed to the simultaneous occurrence of two opposing processes. The potential for an increase in the chain blocking effect is anticipated with the rise in nanoparticle concentration. In a recent study, Wang et al. [101] conducted an investigation into the influence of functionalized Titania nanoparticles on the physical characteristics of the epoxy nanocomposite. Functionalization of nanoparticles was performed by adding a silane coupling agent. The authors revealed that adding TiO_2 will reduce the molecular chain mobility results in an increment in the T_g. An increment of 43% in T_g is reported at 5 wt% nanofiller. Strong interface formation was found to be a major cause of restricted molecular chain movement. Li et. al.[102] considered the influence of adding mesoporous TiO_2 in the epoxy composite electrolyte on electrochemical and mechanical performance. The authors presented that mixing mesoporous TiO_2 destroys the ordered molecular chain of polymer and promotes cross-linking. This happened due to the interaction of TiO_2 with the polar groups of the polymer chain resulting in a decrement in the reorganization of the polymer chain. The authors concluded that adding TiO_2 content up to 6 wt% will increase the compression strength of the composite by 60%. In addition, the use of TiO_2 nanofiller served as a thermal barrier, hence enhancing the heat insulation properties. Marotta et. al. [103] conducted a study on the curing behavior, mechanical characteristics, and thermal properties of nanocomposites consisting of epoxy and TiO_2. According to the authors' findings, the incorporation of nano TiO_2 results in a reduction in the enthalpy of the curing process and induces a shift of the reaction towards a higher temperature. Furthermore, the literature provides an explanation for the dual impact of TiO_2 incorporation, namely, the reduction in the reaction volume of epoxy anhydride and the formation of a novel interaction between TiO_2 and epoxy. These effects together result in a decrease in the degree of crosslinking within the polymer matrix. The literature has shown that there is a reduction in the T_g and a little increase in the mechanical characteristics of the composite. The experimental and predictive investigation conducted by Papanicolaou et al. [104] examined the impact of TiO_2 nanoparticles and microparticles on the flexural strength of epoxy nanocomposites. Composites were prepared by magnetic stirring. SEM images revealed that the formation of micro aggregates is inevitable in the mixing of micro TiO_2. Nano TiO_2 particles showed better particle distribution in the matrix. The authors revealed that adding nano TiO_2 will decrease the flexural modulus for all strain rates applied. This happened due to the delayed cross-linking and creation of filler matrix interface. Nano TiO_2 in limited weight fraction (up to 1%) produces a plasticization effect which produces the rubber-like property in the composite.

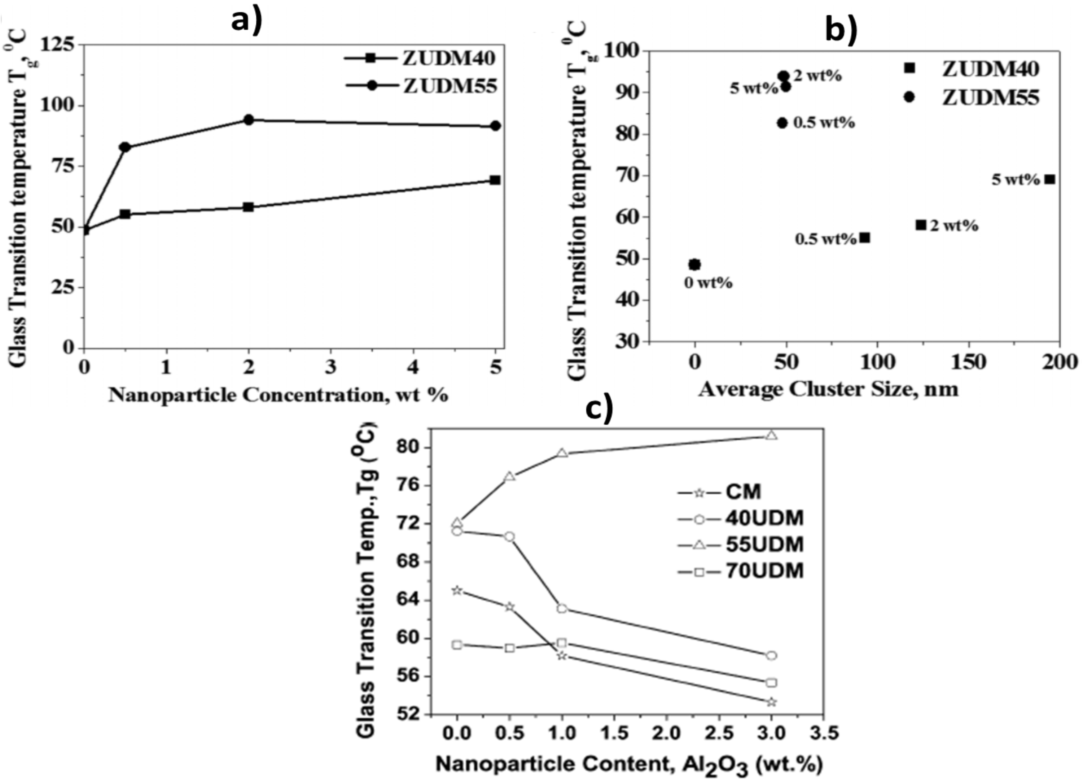

Figure 4. Graphical representation of deviation of T_g for Neat epoxy along with ZUDM40 and ZUDM55 nanocomposite with variation of (a) nanofiller wt% and (b) mean agglomerate dimension. (c) variation of T_g with wt.% of Al_2O_3 at variable UDM parameter; ZUDM40: ZrO_2 / epoxy nanocomposite fabricated by ultrasonication amplitude of 40%; ZrO_2: zirconium dioxide; ZUDM55: ZrO_2/epoxy nanocomposite developed by ultrasonication amplitude of 55% [17]; 40UDM is UDM at vibration of 40% amplitude; 55UDM is UDM processed at 55% amplitude; 70UDM is UDM processed at 70% amplitude [22]

Slika 4. Grafički prikaz devijacije Tg za Neat epoksid zajedno sa nanokompozitom ZUDM40 i ZUDM55 sa varijacijama (a) težinskih % nanopunila i (b) srednje dimenzije aglomerata. (c) varijacija Tg sa tež.% Al2O3 pri promenljivom UDM parametru; ZUDM40: ZrO_2/epoksidni nanokompozit proizveden ultrazvučnom amplitudom od 40%; ZrO_2: cirkonijum dioksid; ZUDM55: ZrO_2/epoksidni nanokompozit razvijen ultrazvučnom amplitudom od 55% [17]; 40UDM je UDM pri vibraciji od 40% amplitude; 55UDM je UDM obrađen na 55% amplitude; 70UDM je UDM obrađen pri 70% amplitude [22]

In another study [17], a variation of T_g with nanoparticle content and average cluster size for ZrO_2-epoxy nanocomposites is shown in Fig. 4a and b respectively, developed by ultrasonication amplitude at 40% (ZUDM40) and 55% (ZUDM55). The monotonically increasing T_g trend is found in ZUDM40 up to 5 wt%. Figure 4c demonstrates that the inclusion of ZrO_2 nanoparticles with a cluster size ranging from 40–50 nm leads to a notable increase in the T_g of ZUDM55. Conversely, a marginal alteration in T_g was observed when incorporating ZrO_2 nanoparticles with a larger average cluster size in ZUDM40. This suggests that higher levels of processing hinder the reduction in T_g at higher particle concentrations. The enhancement of T_g resulting from the addition of 20–30 nm ZrO_2 nanoparticles can be credited to the robust adhesion amongst the nanofiller and the epoxy, which restricts the molecular mobility of the epoxy material under thermal conditions.

The study reveals that comparable patterns may be seen in composites with Al_2O_3 particles with a size of less than 25 nm, embedded in epoxy resin using an advanced ultrasonic dual mixing (UDM) technique. The present research examines the disparity in T_g seen in nanocomposites fabricated by two distinct methods: conventional mixing (CM) and ultrasonic dispersion and mixing (UDM). The investigation focuses on nanocomposites with varying amplitudes of 40%, 55%, and 70%. The UDM has shown optimal outcomes, such as a 26% enhancement in T_g, when operated at an amplitude of 55%, as seen in Figure 3(c). The primary objective of incorporating particles into a polymer matrix is to enhance the cross-linking process by impeding the movement of the epoxy atoms. Nevertheless, the amplification of amplitude by 70% leads to the occurrence of excessive heat, which subsequently results in the breaking of polymer chains and therefore decreases the T_g values [22].

Table 1 summerises the results of recent publications about T_g of oxide nanoparticles reinforced epoxy adhesive.

Table 1. Summary of T_g of oxide nanofiller-epoxy composites
Tabela 1. Rezime Tg kompozita oksidnih nanopunila i epoksida

Development process	Oxide nanofiller				T_g of neat epoxy adhesive (°C)	T_g of nano-composite (°C)	Variation (%)	Ref.
	Type	Diameter (nm)	Concentration					
			(wt.%)	(vol.%)				
Mechanical stirring with heating	TiO_2	25	5		81	116	43	[101]
Ultrasonic cavitation	TiO_2	5	1	-	118	129	9	[33]
Bead-Mill	TiO_2	300	-	8	170	172	0.1	[30]
Shear Mixing & ultrasonic cavitation	TiO_2	50		3	49	52	6	[38]
Optimized ultra-sonication process	TiO_2	~48	10	-	-	-	27	[96]
Ultrasonicated dual mixing	TiO_2	30	1	-	78	82	5	[105]
Ultrasonicated dual mixing	TiO_2 (hybrid)	30	1	-	79	97	23	[106]
Mechanical mixing/ultrasonication	Al_2O_3	78	2	-	59	62	5	[107]
Ultrasonication	Al_2O_3	20	1.25	-	60	70	17	[100]
Planetary centrifugal mixing	Al_2O_3	30	1	-	84	104	23	[108]
Mechanical mixing	Al_2O_3	35	2.5	-	70	78	11	[109]
Mechanical stirring	Al_2O_3	10-30	-	5	83	95	15	[87]
Bead-Mill	Al_2O_3	13	-	5	170	185	9	[30]
Shear mixing	Al_2O_3	45	20	-	112	112	0	[78]
Mechanical mixing and ultrasonication	ZrO_2	45	6	-	61	68	11	[110]
Ultrasonic dual mixing	ZrO_2	30	4	-	181	204	13	[98]
Ultrasonication	ZrO_2	45	6	-	61	70	15	[111]
Ultrasonic dual mixing	ZrO_2	25	2	-	49	94	92	[17]
Mechanical stirring	ZrO_2	15	-	1	50	55	10	[91]
Torus Mill	ZrO_2	12	-	8	100.3	108	8	[47]
Ultrasonication	SiO_2	30	4	-	152	164	8	[112]
Ultrasonication	SiO_2	14	4	-	82	112	36	[113]
Mechanical mixing	SiO_2	270	5	-	228	239	5	[114]
Ultrasonication	SiO_2	15	4	-	62	70	11	[97]
Sonication	SiO_2	100	40	-	~125	~87	-30	[81]

4.2. Effect of Oxide Nanoparticles on Thermal Stability

The use of thermal analysis techniques to assess the thermal deterioration of materials has significant importance in estimating their longevity and durability. The primary weight reduction of epoxy adhesives based on DEGBA typically takes place within the temperature range of 370-420 ^{o}C, mostly as a result of the breakdown of the bisphenol-A [115,116]. The degradation event encompasses a series of sequential steps, including chain scission, char production or carbonization, and char stabilization [117]. As the thermal stability of oxide nanoparticles is very high due to their ceramic nature, therefore in the case of nanoparticulate-epoxy composites, the thermal degradation also follows the same trend as mentioned above for epoxy matrix. Thermal stability of nanocomposites is usually evaluated considering three factors: (1) decomposition temperature (determined from weight loss % of the material with respect to the increase in temperature), (2) activation energy for degradation, and (3) Integral procedural decomposition temperature (IPDT). Several studies have shown improvements in the thermal stability of epoxy matrices with the inclusion of oxide nanoparticles such as TiO_2, Al_2O_3, SiO_2, and ZrO_2. [49,115,118]. A significant increase in decomposition temperature, the activation energy of decomposition, and IPDT has been reported for TiO_2-epoxy and Al_2O_3-epoxy nanocomposites [33,113]. However, a slight improvement in the thermal immovability is reported for ZrO_2-epoxy nanocomposites [49]. The better thermal sustainability of nanoparticulate-epoxy nanocomposites may be credited to the consistent distribution of nanofillers inside the underlying epoxy. The distribution of nanofillers throughout the epoxy base and the presence of a well-defined filler-epoxy boundary contribute to the formation of a heat flow barrier. This barrier is primarily credited to the thermal inertness of oxide nanofillers [115]. The retardant effects of the resultant nanocomposites on heat flow are enhanced as the nanoparticle concentration increases. The quantity of particles has a positive correlation with the concentration of nanoparticles. The augmentation of particle content, coupled with notable clustering, results in a reduction of the cross-linking density. Thermosetting polymers often exhibit a comparatively high degree of cross-linking density, resulting in elevated decomposition temperatures [33]. The optimization of cross-linking density occurs when the epoxy matrix is maintained at its full stoichiometry. Once the stoichiometry of the epoxy resin is disrupted by the introduction of external TiO_2, Al_2O_3, SiO_2, and ZrO_2 nanoparticles, above a critical threshold [49,115,118,119]. the crosslink density diminishes. Consequently, a reduction in crosslink compactness results in reduction in the decomposition temperature.

The observed rise in the activation energy for the disintegration of the nanocomposites may be attributed to the significant structural changes that occur, particularly when the nanoparticles are uniformly dispersed inside the epoxy matrix. In instances when nanoparticles are effectively disseminated inside a matrix, the phenomenon of limitation to random chain scission is intensified due to the greater number of impediments that impede the transport of heat and oxygen through the matrix. However, exceeding a critical threshold of nanoparticle concentration has a negative impact on the activation energy of breakdown.

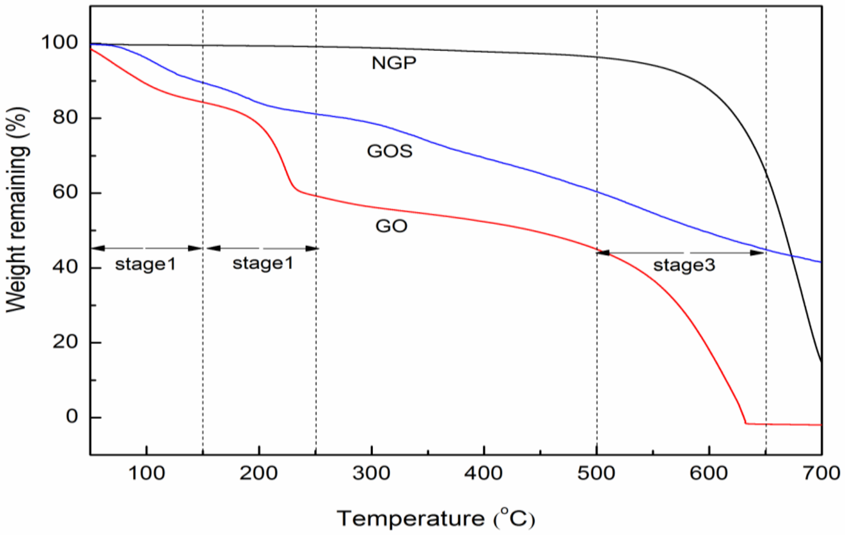

Figure 5. Wt.% v/s Temperature plot of epoxy nanocomposite [121]

Slika 5. Grafik tež. % u odnosu na temperaturu epoksidnog nanokompozita [121]

The relationship between the change in IPDT and the increase in nanoparticle content within the epoxy matrix often differs from that seen for the activation energy of these nanocomposites. The disparity in the physical characteristics of activation energy and the IPDT [120] may account for this phenomenon. The concept of activation energy pertains to the rapid breakdown procedure of the epoxy atom chain, with the exclusion of the early decomposition and char yield creation. On the other hand, the IPDT encompasses the whole constancy of the samples, counting the beginning, rapid decay, and closing char formation stages. The observed trend of increasing IPDT in oxide nanoparticulate-epoxy composites with more nanofiller loading may be credited to this factor. Thus, the inclusion of TiO_2 nanofiller in the epoxy matrix results in better thermal resistivity compared to the neat epoxy adhesive. The introduction of the Al_2O_3 and ZrO_2 nanoparticles into the epoxy resin also enhances thermal resistance because these particles work as virtuous insulators to the heat flow through the matrix [90]. The better thermal resistance by the ZrO_2 nanoparticle may further be supported by their good attachment with the epoxy matrix [30].

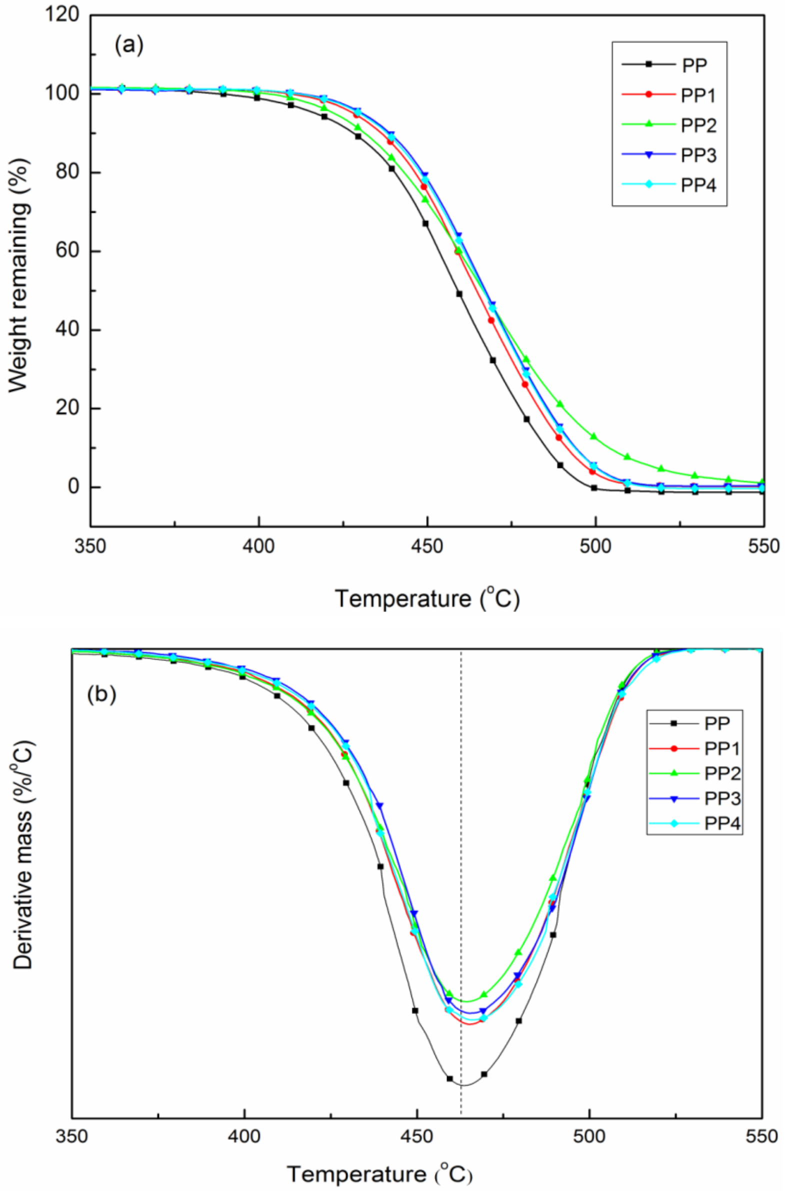

Figure 6. Wt.% vs Temperature plot of epoxy nanocomposite and DTG (b) thermograms wt. loss % vs temperature [121]

Slika 6. Grafik tež.% u odnosu na temperaturu epoksidnog nanokompozita i DTG (b) termogram mas. gubitak % u odnosu na temperaturu [121]

The thermal breakdown curves of natural graphite powder (NGP), graphene oxide (GO), and graphene-SiO_2 hybrids (GOS) were investigated by Bian et al. [121] as seen in Figure 5. The findings indicate that the degradation of GOS exhibits similarities to that of GO, but with a slower degradation rate and a greater accumulation of residual GOS characteristics. This may be attributed to the incorporation of SiO_2. The incorporation of graphene oxide sheets (GOS) into polymer nanocomposites contributes to the enhancement of their thermal characteristics. Figure 6 depicts the thermogravimetric analysis (TGA) and derivative thermos-gravimetric (DTG) curves of hybrid polypropylene/graphene oxide silicon dioxide (PP/GOS) nanocomposites including varying concentrations of graphene oxide SiO_2 (GOS) [121]. The maximum decomposition temperature is found to increase from 454^0C to 462.4^0C for pure PP to GOS/PP (0.5 wt%) nanocomposite respectively.

5. CONCLUSIONS

The performance of oxide nanoparticulate reinforced epoxy nanocomposites is dependent on a wide variety of parameters. These parameters include the category of epoxy resin, size, the type, concentration, and shape of oxide nanofillers, as well as the interface between the nanofillers and the base polymer matrix. The manifold enhancement in the physical, thermal and mechanical properties of polymer nanocomposites can only be achieved if nanoparticles are uniformly dispersed (up to a maximum cluster of 2 to 3 particles) without significant clustering in viscous polymer matrix (epoxy matrix). Multiple processing techniques were used in the past for dispersing nanofillers in the epoxy like polymer matrix. Each method of disagglomerating nanoparticles has its own set of advantages and disadvantages, however, the ultrasonic dual mode mixing approach found out very promising for dispersing nanofillers in polymer matrices even up to the size of individual nanoparticles.

The research results that have been published so far are still insufficient to exhibit a direct link between the physical characteristics of nanoparticulate-epoxy composites and their thermal properties. Because in some cases, all three trends observed using the same nanoparticle with different dispersion scenario in polymer matrix. Based on the dispersion scenario, the physical and thermal properties may increase, decrease and remain unchanged. This has happened because of the way of physical adsorption of polymer layer on the nanoparticle surface. From an industrial perspective, the creation of a more sophisticated material also necessitates the existence of a direct link between the process and the material. To get the most possible advantage from the nanoparticulate-epoxy composites, it is obligatory to do more research in this direction.

Acknowledgements

M.S. Goyat acknowledges the funding by Science and Engineering Research Board (SERB), Department of Science & Technology (DST), India, project number SUR/2022/005356.

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IZVOD

PREGLED POBOLJŠANIH FIZIČKIH I TERMIČKIH SVOJSTAVA EPOKSIDNIH KOMPOZITA OJAČANIH NANOČESTICAMA OKSIDA

Epoksidne smole su dobro poznate zbog svojih poželjnih termičkih i mehaničkih karakteristika u raznim oblastima, uključujući automobilsku, građevinsku i avio-industriju. Međutim, inherentna krhka priroda visoko umreženih epoksidnih smola generalno dovodi do slabosti u otpornosti na stvaranje pukotina i njihovo kretanje. Krhkost epoksidnih smola je jedna od glavnih prepreka koja sprečava njihovu upotrebu u širem obimu. Zbog toga su se mnogi istraživači fokusirali na ojačavanje epoksidnih smola različitim tipovima nanostruktura uključujući ugljenične nanocevi (CNT), organska/neorganska nanopunila da bi se obezbedila veća čvrstoća, bez umanjivanja drugih bitnih termo-fizičkih karakteristika nanokompozita. Većina članaka za pregled fokusiranih na epoksidne kompozite ojačane CNT-om, a dostupni su vrlo ograničeni članci za pregled koji se fokusiraju na epoksidne kompozite ojačane oksidnim nanopunilima. U ovom preglednom članku istraženi su epoksidni nanokompoziti ojačani nanočesticama glinice (Al_2O_3), titanija (TiO_2), silicijum dioksida (SiO_2) i cirkonijum (ZrO_2). Uticaj nanočestica oksida u modifikaciji fizičkih i termičkih osobina epoksidnih nanokompozita je predstavljen, upoređen i kritički analiziran u cilju optimizacije performansi epoksidnih nanokompozita.

Ključne reči: *oksidni nanopunjač; temperatura prelaska stakla; fizička svojstva; termička svojstva; termička degradacija*

Pregledni rad
Rad primljen: 27.09.2023.
Rad prihvaćen: 25.10.2023.
Rad je dostupan na sajtu: www.idk.org.rs/casopis
