

Characteristics of Mechanical Properties and Thermal Behavior of Epoxy Nanocomposites and Coatings by Zinc Borate, Nano Silica, and Hardener

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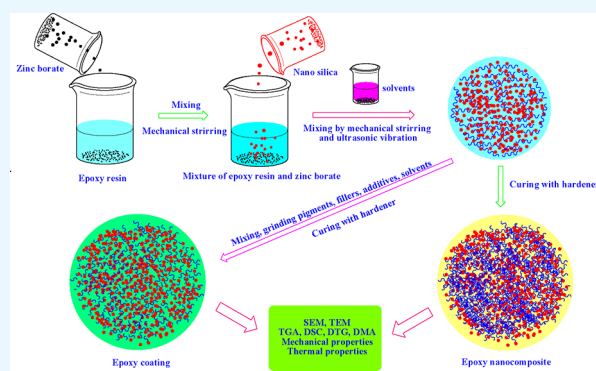
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ABSTRACT: This study reports the ability of zinc borate (ZB) and nano silica (NS) in improving mechanical properties and thermal behavior of nanocomposites and coatings composed of epoxy resin EPIKOTE 1001 × 75 cured with hardener T31. The properties of the fabricated nanocomposites were characterized using scanning electron microscopy, transmission electron microscopy, thermogravimetric analysis, derivative thermogravimetry, differential scanning calorimetry, and dynamic mechanical analysis. With the addition content of 5 wt % ZB into epoxy resin (EPIKOTE 1001 × 75/T31/ZB-5), the impact strength of the fabricated epoxy polymer film increased by 50%, and the glass transition temperature (T_g) increased from 52 to 71 °C. By adding the content of 5 wt % ZB and 1 wt % NS into epoxy resin (EPIKOTE 1001 × 75/T31/ZB-5/NS-1), the impact strength of the formed epoxy nanocomposite films increased by 137.5%, and T_g increased from 52 to 82 °C. The results showed that 5 wt % ZB, 1 wt % NS, and hardener T31 improved the toughness and mechanical properties of epoxy polymer materials. The thermal stability of epoxy composite EPIKOTE 1001 × 75/T31/ZB-5 increased by 1.9% and that of epoxy nanocomposite EPIKOTE 1001 × 75/T31/ZB-5/NS-1 increased by 4.7%. The epoxy coating based on epoxy resin EPIKOTE 1001 × 75/T31/ZB-5/NS-1 achieved mechanical properties and had the strongest decomposition temperature at 642 °C.



1. INTRODUCTION

Epoxy resin with its chemical resistance has been widely used today as anticorrosion coatings for steel structures and thermal equipment. However, epoxy resin has the disadvantage of less toughness. There are many methods to improve the mechanical properties of epoxy resins through hardeners, modifying the main chain, additives, and nanoparticles.^{1,2}

To increase thermal stability and fire resistance of polymers, last studies have focused on using thermal stability enhancers such as halogen compounds, antimony oxide, zinc borate (ZB), and phosphorus compounds.^{3–15} The halogen flame retardant compounds have high flame retardant efficiency,³ but some disadvantages often produce toxic products in the combustion process, so it is currently limited in use.^{4–6} Phosphorus flame retardant compounds, which show high flame retardant efficacy against many environmentally friendly substrates, are being investigated to replace traditional halogen compounds.⁵

ZB is considered a flame retardant and smoke prevention additive and is thermally stable, safe, nontoxic, and anticorrosive during decomposition.^{6–9} Hydrated ZB promotes the formation of a protective coal layer, which acts as a good insulator and protects the substrate underneath from heat and oxygen. It converts the flammable polymer to carbon,

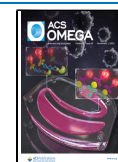
minimizing flue gas emissions burning during the gas-phase reaction.^{10–12} ZB releases water molecules at high temperatures, providing a natural cooling effect.¹³ ZB decomposes causing dehydration, endothermically absorbs heat from vaporized water, and locally dilutes oxygen and combustible gas components.¹⁴ ZB during the condensation phase produces fatty hydrocarbons rather than benzene and other aromatics that increase cross-linking reactions within the polymer, preventing smoke during combustion, thus improving thermal stability, reducing soot formation leading to low smoke generation, and preventing combustion.¹⁵

In recent times, nanocomposite materials have been studied and applied quite commonly.^{16–26,30} In the study,¹⁶ the authors used epoxy resin EPON 828 and a content of 5–10 wt % nano silica (NS) (Aerosil R974) to form a nanocomposite. NS is modified with silane compounds that increase the ability

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to bind with polymer matrix.¹⁷ In the study,¹⁸ the authors studied liquid epoxy resin modified with 0–3 wt % NS Aerosil R200, increasing the mechanical properties and the T_g . The mechanical properties of the material were enhanced by NS on epoxy resin DER 671 × 75/Epicure 3125.¹⁹ Composite materials based on epoxy resin reinforced with 5–7 wt % nano clay increased mechanical properties.²⁰ Epoxy resin was modified with unsaturated polyester resin and NS which improved the impact strength of the epoxy coating significantly.²¹ Nanocomposites of surface-modified ZB/polypropylene were prepared, and their mechanical properties were measured. The results suggested that the mechanical properties of ZB/polypropylene composites were improved.²² The modified commercial-grade polyurethane coatings containing TiO₂ nanocomposites show better properties, including hydrophilicity, degradation of organic pollutants, antibacterial activity, and water resistivity, compared to unmodified commercial-grade polyurethane coatings.²³ Epoxy coatings were reinforced with several nanoparticles, such as nano-SiO₂, nano-Fe₂O₃, nano clay, and nano-TiO₂, that the results improved cross-link density, increased the glass transition temperature (T_g), and improved the impact strength of the epoxy coating significantly.²⁴ Epoxy resin nanocomposites reinforced with silica nanoparticles have been prepared at different nanoparticle loading levels. The surface functionality of the silica nanoparticles is manipulated by the phosphoric acid (H₃PO₄)-doped conductive polyaniline via a surface-initiated polymerization method. The improved glass transition temperature (T_g) and enhanced mechanical properties of the cured epoxy resin nanocomposites filled with the functionalized silica nanoparticles were observed compared with those of the cured pure epoxy resin.²⁵

In the study,²⁶ the impact strength of the polymer film based on epoxy resin DER 671 × 75/hardener T31 increased by 125%, and the thermal stability increased by 45.35% with a content of 5 wt % triphenyl phosphate and 1 wt % NS (fumed silica S5505).

Liquid epoxy resin EPIKOTE 1001 × 75 has two epoxy groups at the beginning and the end of the chain. The curing reaction of the epoxy resin occurs when the epoxy group reacts with active hydrogen to open the epoxy group ring. The active hydrogen-containing compounds used to cure epoxy resin are amines, polyamides, phenolic resins, modified phenolics, amine adducts, Mannich Base, etc.^{27,28} Hardener T31 was used to cure epoxy resin E44 at room temperature.²⁸

Based on previous studies, a new idea of combining ZB as a flame retardant, NS, and hardener in epoxy nanocomposites was formed. In this work, the effects of ZB, NS, and hardener T31 on the mechanical properties and thermal behavior of epoxy polymer composite EPIKOTE 1001 × 75/hardener T31 were studied and applied to epoxy coatings.

2. EXPERIMENTAL SECTION AND METHODS

2.1. Materials. The liquid epoxy resin was used for this study with the trade name EPIKOTE 1001 × 75 (Manufacturer of Hexion Chemicals). Epoxy resin EPIKOTE 1001 × 75 has a content of 75 wt % solid, dissolves in solvent xylene, and has an epoxy equivalent weight of 450–500 g/equiv. The hardener for epoxy resin is T31 (Zhenjiang Danbao Resin manufacturer, China) with an amine number of 450–550 mg KOH/g. NS (fumed silica, S5505 Sigma) and ZB as a flame retardant were used. Pigments for coating include iron oxide, zinc chromate, and talc filler (China). Solvents dissolve

epoxy resin and adjust the viscosity for coating including xylene, toluene, and acetone (China).

2.2. Preparation of Samples. **2.2.1. Dispersion of ZB and NS in Epoxy Resin EPIKOTE 1001 × 75.** ZB was dispersed in epoxy resin EPIKOTE 1001 × 75 by the mechanical stirring method. 2.5 g of ZB and 50.0 g of epoxy resin EPIKOTE 1001 × 75 were weighed with a content of 5 wt % ZB. The mixture was poured into a 100 mL beaker and stirred at 500 rpm for 10 min and then gradually increased the stirring speed to 1000 rpm and maintained for 15 min. Finally, the stirring speed of the mixture was increased to 2000 rpm and kept for 60 min. The samples were studied with the contents of 3, 5, and 7 wt % in epoxy resin EPIKOTE 1001 × 75 and were denoted as EPIKOTE 1001 × 75/ZB-3, EPIKOTE 1001 × 75/ZB-5, and EPIKOTE 1001 × 75/ZB-7, respectively.

NS was dispersed in epoxy resin EPIKOTE 1001 × 75 by the mechanical stirring method combined with ultrasonic vibration. 0.5 g of NS was weighed into a 250 mL beaker containing 2.5 g of acetone solvent and stirred at 250 rpm for 15 min. Next, 50.0 g of epoxy resin EPIKOTE 1001 × 75 was added to the mixture with the content of 1 wt % NS in epoxy resin EPIKOTE 1001 × 75. The stirring speed of the mixture was increased to 2000 rpm and was maintained for 45 min. Finally, the mixture was sonicated for 45 min to form a sample of epoxy resin EPIKOTE 1001 × 75/NS-1.

Epoxy resin EPIKOTE 1001 × 75/ZB/NS was also prepared by mechanical stirring and ultrasonic vibration. First, NS was predispersed in epoxy resin EPIKOTE 1001 × 75. Then, ZB was dispersed in the mixture of epoxy resin EPIKOTE 1001 × 75/NS to form a sample of epoxy resin EPIKOTE 1001 × 75/ZB/NS.

2.3. Analytical Devices and Methods for the Analysis of Polymer Composite Materials. Analytical devices include the mechanical stirrer (model IKA-RW 20, Germany) and ultrasonic device (Vibra-Cell, model CV334, USA). The gel content of polymer composite samples was determined by extraction with acetone solvent in the Soxhlet kit for 12 h. Transmission electron microscopy (TEM) images were scanned using the TEM Jeol machine (model JEM 1400, Japan). Scanning electron microscopy (SEM) images were scanned using the SEM Jeol machine (model JSM-IT 200, Japan). The thermal behavior of polymer composite materials was characterized by thermogravimetry–differential scanning calorimetry–derivative TG (TG–DSC–DTG) on Setaram Labsys Evo (TG–DSC 1600 °C). Dynamic mechanical analysis was tested on dynamic mechanical analysis (DMA) equipment Q800 (TA Instruments). The mechanical properties of polymer films and coating films were determined through the parameters of flexibility, pencil hardness, adhesion, and impact strength. The impact strength of polymer films was determined according to the ISO 6272:2002 standard (Erichsen equipment, model 304) using mechanical force from a 1.00 kG dumbbell at the maximum height of free fall onto the specimen without damaging the polymer films. The flexibility of polymer films was determined according to the ISO 1519:2002 standard (Erichsen equipment, model 266); polymer films were bent through the shaft with the smallest diameter without damaging the films. The pencil hardness of polymer films was determined according to the JIS K5400-90 standard, which was the hardness of a pencil in front of a pencil that scratched the films. The adhesion of polymer films was determined according to the ASTM D3359-93 standard (Erichsen equipment, model 295). Dry film thickness is

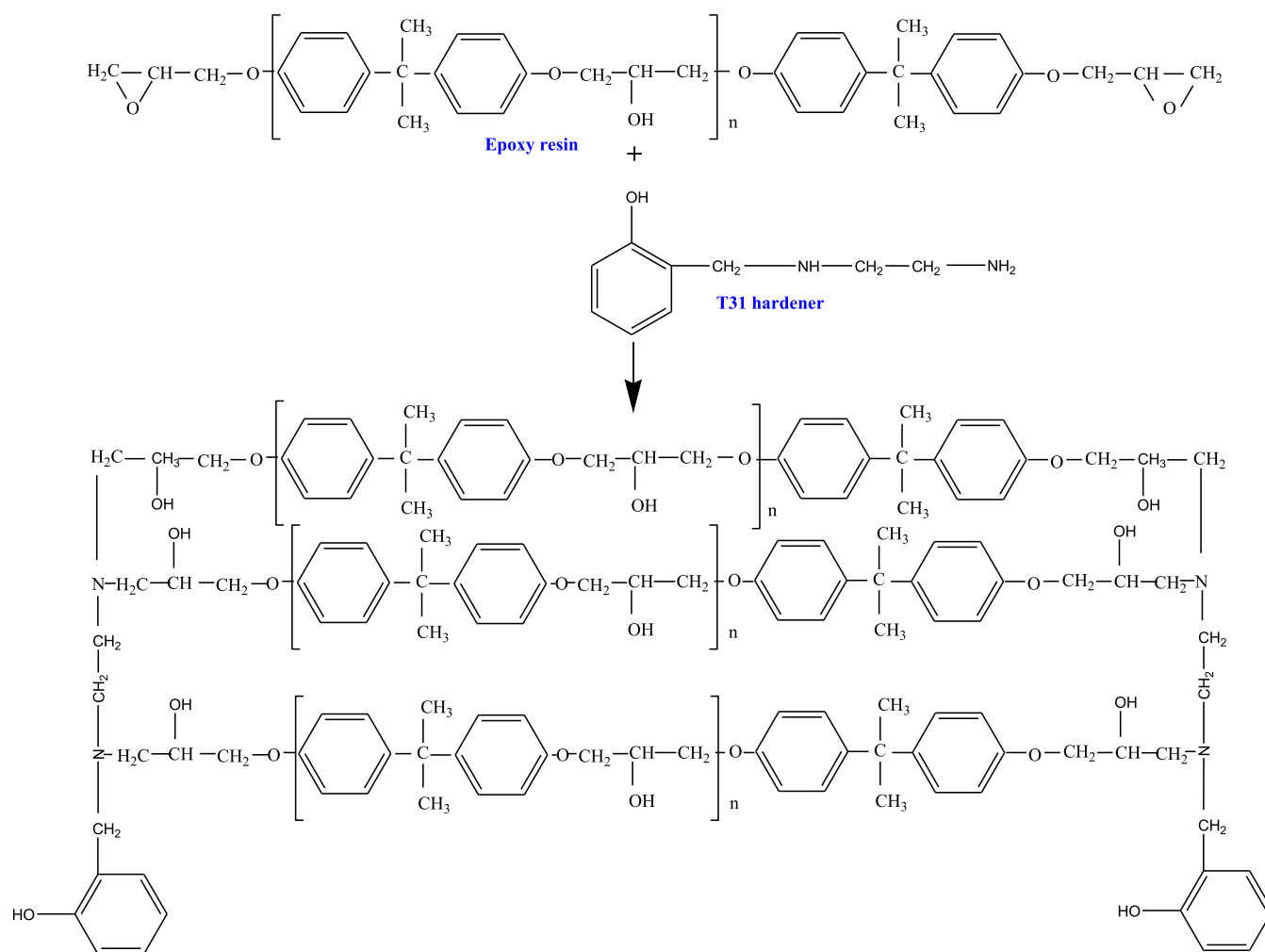


Figure 1. Curing reaction between epoxy resin EPIKOTE 1001 × 75 and hardener T31.

determined by the Vietnam National TCVN 9406: 2012 standard (MiniTest 3100) using an electronic dry film thickness gauge with a magnetic induction probe for magnetic metal substrates such as iron and steel.

3. RESULTS AND DISCUSSION

3.1. Effects of Hardener T31 on the Curing Degree, Mechanical Properties, and Thermal Behavior of Epoxy Polymer Composite EPIKOTE 1001 × 75/T31. The curing reaction between epoxy resin EPIKOTE 1001 × 75 and hardener T31 occurs as follows (Figure 1).

The curing reaction from Figure 1 shows that the epoxy resin after curing has a 3D network structure; the ether group of epoxy resin reacts with active hydrogen of hardener T31, opening the epoxy ring to form many hydroxyl groups that increase the adhesion of materials. In the main chain, there are many aromatic rings from epoxy resin EPIKOTE 1001 × 75 and hardener T31. These aromatic rings increase the thermal stability of epoxy composite materials.

The degree of reactivity between the ether group of the epoxy resin and the active hydrogen in the amine group of the hardener affects the 3D structure of the epoxy resin after curing and thus affects the properties of the epoxy material.

The degree of curing between epoxy resin and hardener T31 is determined through the gel content. The gel content of the polymer is the part of the 3D thermoset structure that is not

extracted in the acetone solvent. The higher the curing density, the higher the gel content and the better the mechanical properties of the epoxy polymer material. Therefore, it is necessary to have a suitable reaction ratio between the hardener and the epoxy resin to achieve the highest gel content.

In the study,²⁶ hardener T31 was used for curing epoxy resin DER 671 × 75 with the content of 30 wt %. Therefore, hardener T31 was investigated with the contents of 22, 27, and 33 wt % in epoxy resin EPIKOTE 1001 × 75. Figure 2 presents the results for the gel content (%) of the samples.

The results from Figure 2 show that if the contents of hardener T31 are 22, 27, and 33 wt %, the epoxy polymer composite sample has the gel contents of 50, 90, and 70%, respectively.

The epoxy polymer composite sample achieved the gel content of 50% with a content of 22 wt % hardener T31. Because the amount of hardener T31 is not enough to bond the epoxy resin to form a thermoset structure, the curing density is low, so the gel content is low.

The epoxy polymer composite sample achieved the gel content of 70% with a content of 33 wt % hardener T31. This result is due to an excess of hardener T31 and a lack of epoxy resin. Therefore, the curing density is low, and the gel content is also low.

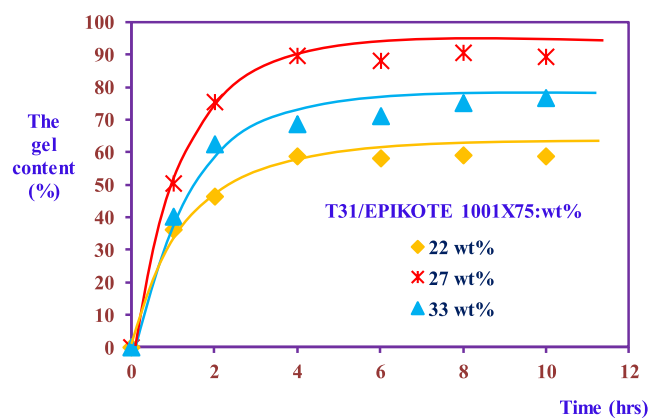


Figure 2. Gel content (%) of epoxy polymer composite EPIKOTE 1001 \times 75/T31 cured at room temperature.

The epoxy polymer composite sample achieved the highest gel content of 90% with a content of 27 wt % hardener T31. The amount of the curing agent is just enough for the curing reaction to occur with the highest curing density.

The above results show that the suitable hardener content is 27 wt % to achieve the highest curing density.

3.1.1. Mechanical Properties of the Epoxy Polymer Film EPIKOTE 1001 \times 75/T31. The mechanical properties of the epoxy polymer film EPIKOTE 1001 \times 75/T31 are shown in Table 1.

The epoxy polymer film was coated on steel with a standard dry film thickness of 70–90 μm and allowed to stabilize for at least 48 h before the mechanical properties were determined.

The results from Table 1 show that the mechanical properties of the epoxy polymer film EPIKOTE 1001 \times 75/T31 such as flexibility, adhesion, and pencil hardness reach 2 mm, 5B, and 5H, respectively. These properties meet standard for coatings.³¹ However, the impact strength of the epoxy polymer film is only 20 kG cm. The impact strength of polymer films is required to be at least 45 kG cm for coating.³¹ Thus, it can be seen that the cured epoxy film EPIKOTE 1001 \times 75/T31 is quite hard and brittle due to the enhancement of aromatic rings from the hardener T31. Although, the curing density between the curing agent and the epoxy resin reached the highest gel content of 90% (Figure 2). However, there may still be areas that do not form 3D structure in the epoxy polymer composite EPIKOTE 1001 \times 75/T31. Therefore, it is necessary to further improve the bonding ability between the epoxy resin and the hardener through nanoparticles and thereby increase the impact strength of the epoxy polymer film. Nanoparticles have been known to have many advantages in enhancing the mechanical properties of polymer materials.^{16–26,30}

3.2. Thermal Behavior of Epoxy Polymer Composite EPIKOTE 1001 \times 75/T31. The thermal properties of epoxy polymer composite EPIKOTE 1001 \times 75/T31 were evaluated by TG–DTG–DSC analysis. The results are presented in Figure 3.

The results from Figure 3a show that the epoxy polymer composite EPIKOTE 1001 \times 75/T31 loses 5 wt % at a

temperature range of 100–197 $^{\circ}\text{C}$, which is the solvent evaporation. The sample decomposes by 20 wt % at a temperature range of 100–337 $^{\circ}\text{C}$, and the sample decomposes by 50 wt % at a temperature range of 100–380 $^{\circ}\text{C}$. The final decomposition temperature is 450–800 $^{\circ}\text{C}$. The strongest decomposition temperature on the DTG curve is 363 $^{\circ}\text{C}$, and the remaining TG is 66.581 wt % with the highest decomposition rate of $-8.49\%/min$.

The thermal properties of polymer materials can be evaluated based on the decomposition temperature of the polymer sample. The decomposition temperature of epoxy polymer composite EPIKOTE 1001 \times 75/T31 is quite high (the strongest decomposition temperature is 363 $^{\circ}\text{C}$). The thermal decomposition property of epoxy polymer composite EPIKOTE 1001 \times 75/T31 is higher than 300 $^{\circ}\text{C}$ because the structure of epoxy polymer material EPIKOTE1001 \times 75/T31 has high crosslink density, and the chemical composition of hardener T31 has many aromatic rings, which improves the thermal stability of epoxy polymer composite EPIKOTE 1001 \times 75/T31.

In Figure 3b, the DSC curve records the differential heat flow energy of the sample that changes with temperature, which characterizes the reactions occurring, including the glass transitions, curing, and decomposition processes. The highest energy peak forms at a temperature of 363 $^{\circ}\text{C}$, representing the strongest thermal decomposition. The results on the DSC curve are completely consistent with the results of the TG–DTG analysis.

Thus, the analysis results from Figures 1–3 show that the hardener T31 affects the structure and thermomechanical properties of epoxy composite material EPIKOTE 1001 \times 75/T31. In general, the hardener T31 increases the number of aromatic rings in the structure and increases the crosslinking density in the 3D structure. Therefore, the thermal stability of the epoxy composite EPIKOTE 1001 \times 75/T31 is good. However, the low impact strength of epoxy composite material EPIKOTE 1001 \times 75/T31 needs to be further improved.

3.3. Effects of ZB on the Mechanical Properties and Thermal Behavior of Epoxy Polymer Composite EPIKOTE 1001 \times 75/T31/ZB. **3.3.1. Dispersion of ZB in Epoxy Resin EPIKOTE 1001 \times 75.** The sample was studied with the content of 5 wt % ZB in epoxy resin EPIKOTE 1001 \times 75. The SEM images of epoxy polymer composite EPIKOTE 1001 \times 75/T31/ZB-5 are shown in Figure 4.

The SEM images from Figure 4 show that ZB is well dispersed in epoxy resin EPIKOTE 1001 \times 75/T31. Because of the monocrystalline structure of ZB with hydrogen bonding in the structure, ZB is easily dispersed in epoxy resin by mechanical stirring. Figure 4 also shows that the ZB crystals are evenly dispersed and separated on epoxy resin.

3.3.2. Mechanical Properties of Epoxy Polymer Film EPIKOTE 1001 \times 75/T31/ZB. The samples were studied with the contents of 3, 5, and 7 wt % ZB in epoxy resin EPIKOTE 1001 \times 75.

The mechanical properties of epoxy polymer films EPIKOTE 1001 \times 75/T31/ZB are shown in Table 2.

Table 1. Mechanical Properties of Epoxy Polymer Film EPIKOTE 1001 \times 75/T31

| sample | polymer | dry film thickness (μm) | impact strength (kG cm) | flexibility (mm) | pencil hardness | adhesion |
|--------|------------------------------------|--------------------------------------|-------------------------|------------------|-----------------|----------|
| Ep0 | Epoxy EPIKOTE 1001 \times 75/T31 | 87.26 | 20 | 2 | 5H | 5B |

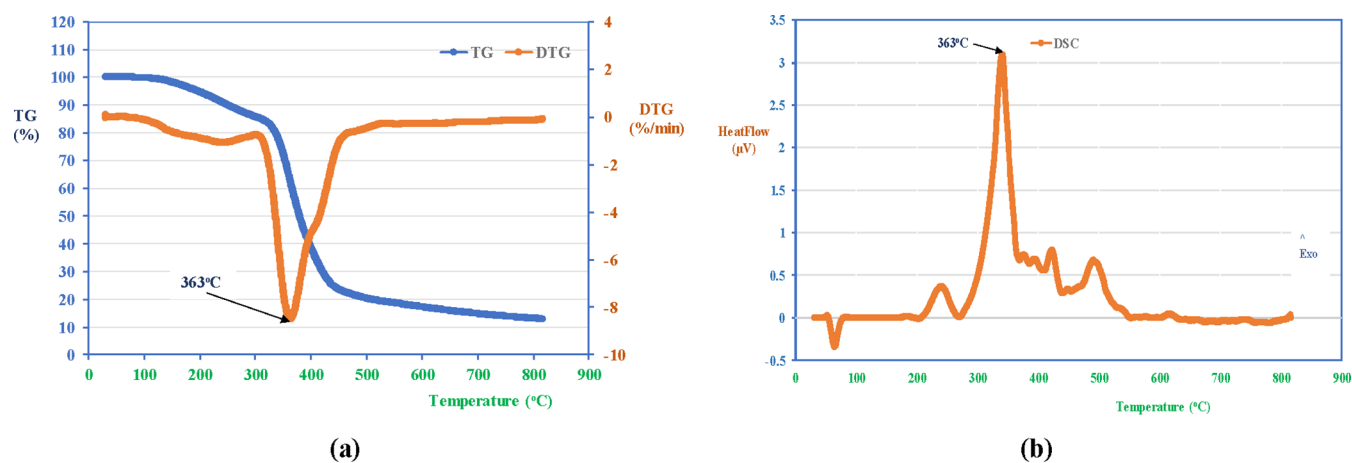


Figure 3. TG–DTG curve (a) and DSC curve (b) of epoxy polymer composite EPIKOTE 1001 × 75/T31.

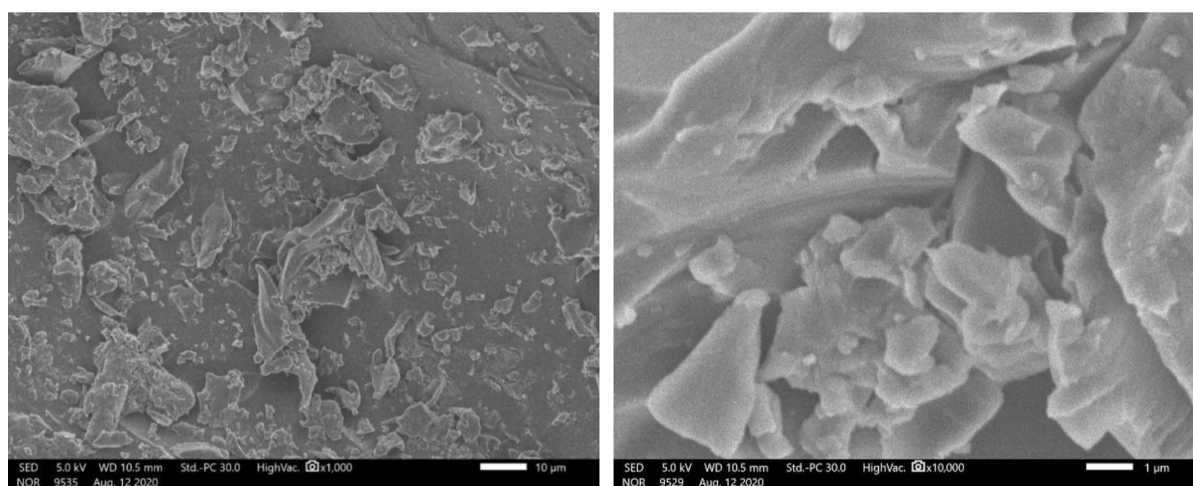


Figure 4. SEM images of epoxy polymer composite EPIKOTE 1001 × 75/T31/ZB-5.

Table 2. Mechanical Properties of Epoxy Polymer Films EPIKOTE 1001 × 75/T31/ZB

| sample | polymer | dry film thickness (µm) | impact strength (kG cm) | flexibility (mm) | pencil hardness | adhesion |
|--------|----------------------------------|-------------------------|-------------------------|------------------|-----------------|----------|
| Ep0 | Epoxy EPIKOTE 1001 × 75/T31 | 87.26 | 20 | 2 | 5H | SB |
| Ep3ZB | Epoxy EPIKOTE 1001 × 75/T31/ZB-3 | 89.66 | 22.5 | 2 | 5H | SB |
| Ep5ZB | Epoxy EPIKOTE 1001 × 75/T31/ZB-5 | 87.3 | 30 | 2 | 5H | SB |
| Ep7ZB | Epoxy EPIKOTE 1001 × 75/T31/ZB-7 | 85.33 | 25 | 2 | 5H | SB |

The results from Table 2 show the effect of ZB content on the mechanical properties of epoxy polymer film EPIKOTE 1001 × 75/T31. While adding the contents of 3, 5, and 7 wt % ZB in epoxy resin EPIKOTE 1001 × 75, the impact strength of epoxy polymer film EPIKOTE 1001 × 75/T31 increased from 20 to 22.5 kG cm (sample Ep3ZB), 30 kG cm (sample Ep5ZB, increased by 50%), and 25 kG cm (sample Ep7ZB). The impact strength of epoxy polymer film EPIKOTE 1001 × 75/T31/ZB-5 is the best with the addition of the content of 5 wt % ZB.

The epoxy polymer composite EPIKOTE 1001 × 75/T31 is very brittle and hard because there are many aromatic rings in the structure and there is no bonding filler to reduce the force effect, so the impact strength is low. ZB structure with hydrogen bonding increases the bond between epoxy resin and hardener T31. ZB also serves as a filler in epoxy composite materials. The content of 5 wt % ZB in epoxy resin EPIKOTE 1001 × 75 is suitable for increasing the bonding ability

between epoxy resin, hardener, and ZB filler. Other mechanical properties of the epoxy polymer film EPIKOTE 1001 × 75/T31/ZB-5 from Table 2 are up to the standards for the coating film. The epoxy polymer composite EPIKOTE 1001 × 75/T31/ZB-5 achieved the best mechanical properties, so this sample is also used to study the thermal properties of the material.

3.3.3. Thermal Behavior of Epoxy Polymer Composite EPIKOTE 1001 × 75/T31/ZB. The thermal properties of the epoxy polymer composite EPIKOTE 1001 × 75/T31/ZB-5 were determined by TG–DTG analysis. The TG–DTG curve of epoxy polymer composite EPIKOTE 1001 × 75/T31/ZB-5 is shown in Figure 5.

The results from Figure 5 show that the epoxy polymer composite EPIKOTE 1001 × 75/T31/ZB-5 loses 5 wt % at the temperature range of 100–260 °C. The sample decomposes 20 wt % at a temperature of 352 °C. The sample decomposes 50 wt % at a temperature of 388 °C. The

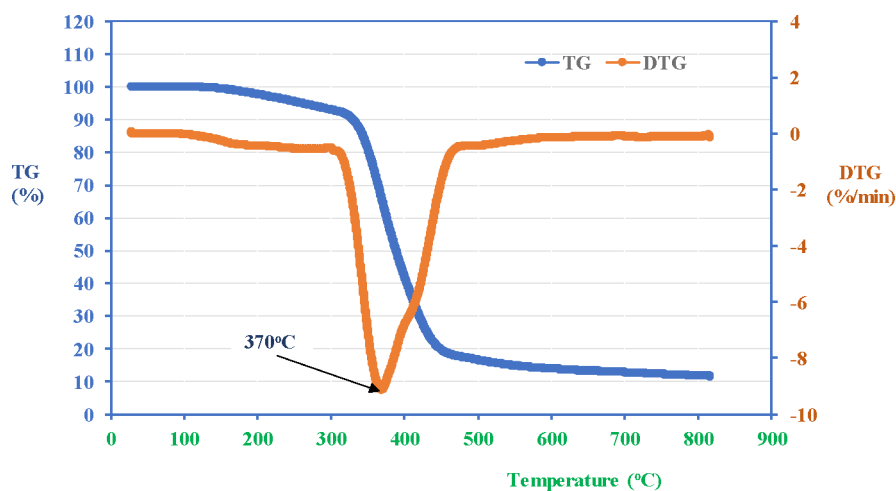


Figure 5. TG–DTG curve of epoxy polymer composite EPIKOTE 1001 × 75/T31/ZB-5.

strongest decomposition temperature is 370 °C with a decomposition rate of $-9.15\%/min$.

The chemical formula of ZB is shown in Figure 6.

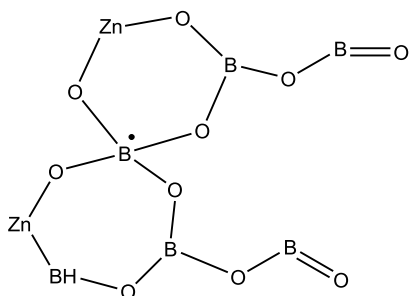


Figure 6. Chemical formula of ZB.

According to the study,¹⁰ the thermal degradation of ZB was severe above 400 °C and occurred in two steps: the first step from 300 to 360 °C corresponded to a weight loss of 5 wt % and the second step from 360 to 430 °C led to a stable material temperature (with the content of 88% original weight). The content of 12 wt % loss could be attributed to reactive dehydration: $ZB \rightarrow 2ZnO \cdot 3B_2O_3 + H_2O$.

The dehydration of ZB began when heated above 290 °C. The thermal decomposition of ZB involved three endothermic phenomena. First, condensation of the B–OH groups due to the loss of three equivalent moles of water produces a large amount of the amorphous material of the $2ZnO \cdot 3B_2O_3$ component. It then decomposed thermally, undergoing crystallization and forming two phases of anhydrous ZB, $3ZnO \cdot B_2O_3$ and $4ZnO \cdot 3B_2O_3$, presumably in the presence of liquid B_2O_3 . ZB decomposed severely above 400 °C.⁹

The strongest decomposition temperature of the epoxy polymer composite EPIKOTE 1001 × 75/T31/ZB-5 was higher than that of the epoxy polymer composite EPIKOTE 1001 × 75/T31, increased from 363 to 370 °C (increased by 1.9%). Thus, ZB with the content of 5 wt % increased the thermal stability of epoxy polymer composite EPIKOTE 1001 × 75/T31/ZB-5. ZB during the condensation phase increased crosslinking reactions in the polymer, prevented smoke during combustion, thus improved thermal stability, reduced soot formation leading to low smoke generation, and prevented combustion.¹⁵ The monocrystalline structure of ZB $Zn-[B_3O_4(OH)_3]$ illustrated a complex network of polytriborate chains. Figure 6 shows that zinc atoms were attached to the network through coordination and further integrated by hydrogen bonding. Hydrogen bonding enhanced the thermal stability of this compound.²⁹

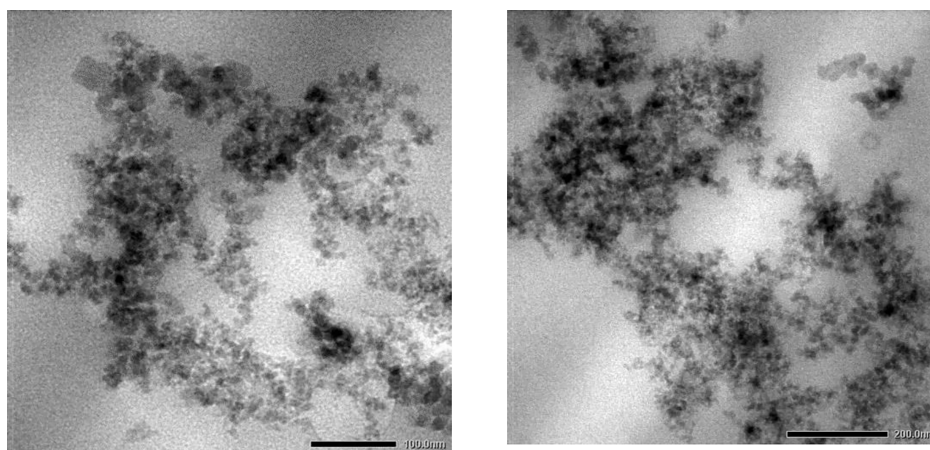
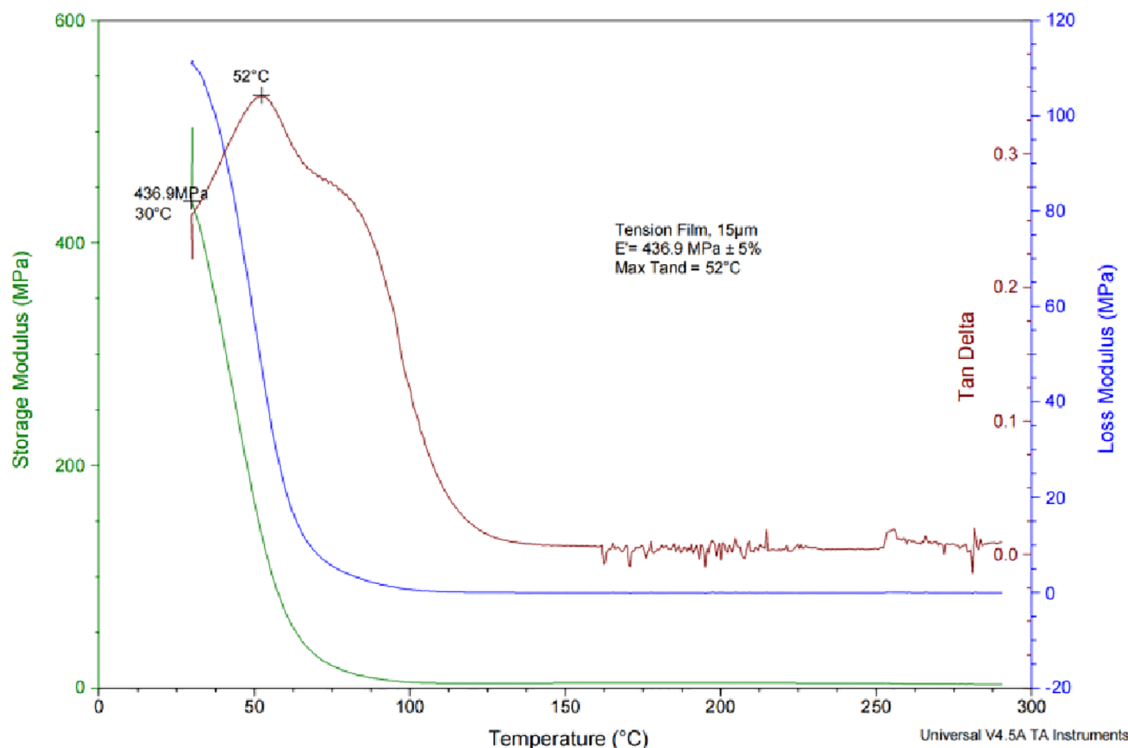


Figure 7. TEM images of epoxy polymer nanocomposite EPIKOTE 1001 × 75/T31/NS-1.

Table 3. Mechanical Properties of Epoxy Polymer Films EPIKOTE 1001 × 75/T31/ZB-5/NS-1

| sample | polymer | dry film thickness (μm) | impact strength (kG cm) | flexibility (mm) | pencil hardness | adhesion |
|---------|---------------------------------------|--------------------------------------|-------------------------|------------------|-----------------|----------|
| Ep0 | Epoxy EPIKOTE 1001 × 75/T31 | 87.26 | 20 | 2 | 5H | 5B |
| EpSZB | Epoxy EPIKOTE 1001 × 75/T31/ZB-5 | 87.3 | 30 | 2 | 5H | 5B |
| EpSZBNS | Epoxy EPIKOTE 1001 × 75/T31/ZB-5/NS-1 | 89.2 | 47.5 | 2 | 5H | 5B |

**Figure 8.** DMA diagram of epoxy polymer composite EPIKOTE 1001 × 75/T31.

3.4. Effects of ZB and NS on the Mechanical Properties and Thermal Behavior of Epoxy Polymer Composite EPIKOTE 1001 × 75/T31/ZB/NS. **3.4.1. Mechanical Properties of Epoxy Polymer Films EPIKOTE 1001 × 75/T31/ZB/NS.** Previous studies have shown that the epoxy polymer composite enhanced the mechanical and thermal properties at a suitable NS content.^{16,18,19,26} In the study,¹⁹ the optimal NS content was 1 wt % which increased the mechanical properties of epoxy resin DER 671 × 76/Epicure 3125. Therefore, NS with the content of 1 wt % was used to increase the mechanical properties and thermal stability for epoxy polymer composite EPIKOTE 1001 × 75/T31.

The TEM images of the epoxy polymer nanocomposite EPIKOTE 1001 × 75/T31/NS-1 are shown in Figure 7.

The TEM images from Figure 7 show that the fabricated epoxy material EPIKOTE 1001 × 75/T31/NS-1 has a nanocomposite structure. The NS particles were separated and well dispersed in the epoxy resin EPIKOTE 1001 × 75/T31. Thus, the method of dispersion by mechanical stirring and ultrasonic vibration is suitable and gives a good dispersion effect of NS in epoxy resin. However, the TEM images also show that the NS particles are of unequal size in the epoxy polymer. There are regions of NS particles that coalesce into larger particles.

The structure of NS is a 3D network, and silanol groups (Si–OH) and siloxane groups (Si–O–Si) are generated on the NS surface. Due to the presence of silanol groups and

siloxane groups on the surface, the silica particles can absorb moisture and easily agglomerate at room temperature. The silanol groups on the surface of adjacent silica particles aggregate by hydrogen bonding and tend to cause the silica particles to clump together into larger particles. Therefore, to reduce the possibility of agglomeration of silica particles, as well as to increase the ability to bind with the polymer matrix, NS is often modified with silane compounds.^{17,19} Silane compounds have strongly polar amine groups, making it easy to bond with the polymer matrix.

3.4.2. Mechanical Properties of Epoxy Polymer Films EPIKOTE 1001 × 75/T31/ZB-5/NS-1. The content of 5 wt % ZB is suitable to reinforce the epoxy polymer composite EPIKOTE 1001 × 75/T31 according to the results of Section 3.4.2 given above. The effects of NS and ZB on the mechanical properties and thermal stability of epoxy polymer composite EPIKOTE 1001 × 75/T31 were studied with the content of 1 wt % NS and 5 wt % ZB.

The mechanical properties of epoxy polymer films EPIKOTE 1001 × 75/T31/ZB-5/NS-1 are presented in Table 3.

The results from Table 3 show that the mechanical properties of epoxy polymer film EPIKOTE 1001 × 75/T31/ZB-5/NS-1 are good. The impact strength of the epoxy polymer film EPIKOTE 1001 × 75/T31/ZB-5 increased from 20 to 30 kG cm with the content of 5 wt % ZB (increased by 50 %) and increased to 47.5 kG cm with the addition content

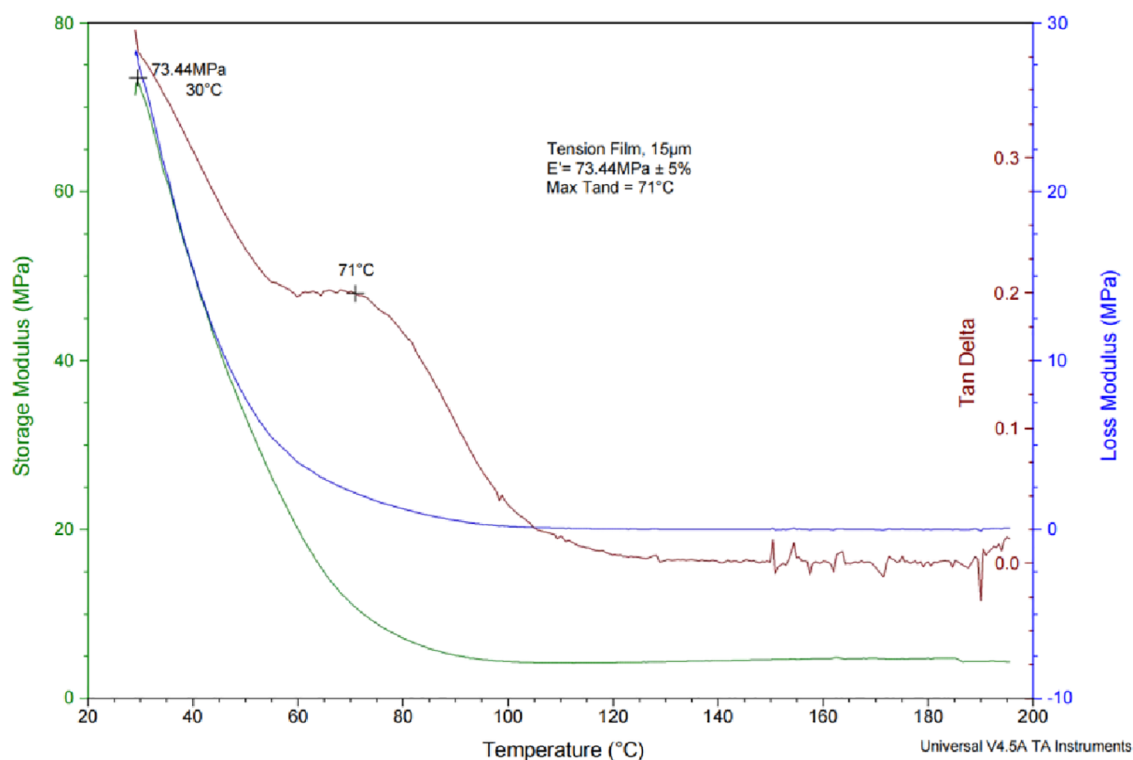


Figure 9. DMA diagram of epoxy polymer composite EPIKOTE 1001 \times 75/T31/ZB-5.

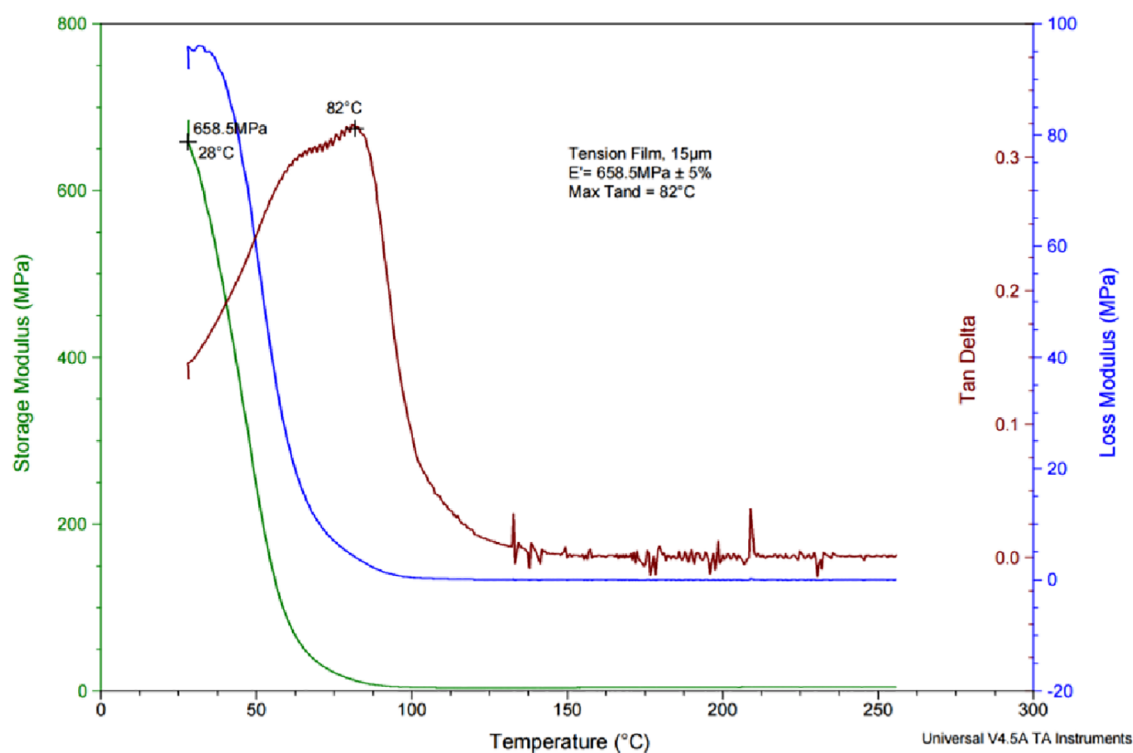


Figure 10. DMA diagram of epoxy polymer composite EPIKOTE 1001 \times 75/T31/ZB-5/NS-1.

of 5 wt % ZB and 1 wt % NS (sample Epoxy EPIKOTE 1001 \times 75/T31/ZB-5/NS-1, increased by 137.5%). NS increased the mechanical properties of polymers that have been demonstrated in previous studies.^{16,19,21,24,26} The nano effect increases the interaction and bonding between the epoxy resin, hardener, and ZB. NS also enhances the dispersion

between components in epoxy nanocomposites and increases the toughness of epoxy nanocomposites.

3.4.3. Dynamic Mechanical Analysis of Epoxy Polymer Nanocomposite. The dynamic mechanical properties of the epoxy polymer composite were characterized by DMA. The DMA analysis records the variation in the storage modulus, loss modulus, and tan delta of the polymer sample with

temperature. Tan delta is the value of the ratio between the loss modulus and the storage modulus. The glass transition temperature (T_g) is determined at the maximum point of the tan delta value.

Determination of the glass transition temperature (T_g) of the epoxy polymer composite is shown in Figures 8–10 and Table 4.

Table 4. Glass Transition Temperature (T_g) of Epoxy Polymer Composites

| polymer | glass transition temperature T_g (°C) |
|---------------------------------------|---|
| Epoxy EPIKOTE 1001 × 75/T31 | 52 |
| Epoxy EPIKOTE 1001 × 75/T31/ZB-5 | 71 |
| Epoxy EPIKOTE 1001 × 75/T31/ZB-5/NS-1 | 82 |

Figures 8–10 and Table 4 show that the T_g of epoxy polymer composite samples gradually increased from 52 °C (EPIKOTE 1001 × 75/T31) to 71 °C (EPIKOTE 1001 × 75/T31/ZB-5) and 82 °C (EPIKOTE 1001 × 75/T31/ZB-5/NS-1), demonstrating the improvement and enhancement in the toughness of epoxy polymer materials. Thus, the content of 5 wt % ZB and 1 wt % NS improved the toughness and enhanced the impact strength of materials. The results are consistent with Section 3.4.3 and Table 3.

The results from Table 4 can be explained as follows: the bonding between epoxy resin and hardener (Figure 1) is a chemical reaction between the epoxy group and amine group with active hydrogen. The reaction between epoxy resin and hardener happens without the participation of fillers. Therefore, the crosslinking density in the 3D structure of epoxy polymer EPIKOTE 1001 × 75/T31 is low, and the T_g (corresponding to max Tan Delta) is as low as 52 °C. The DSC curve (Figure 3b) also shows the vitrification transition temperature at about 52 °C. The epoxy resin is reinforced with 5 wt % ZB, where ZB acts as a filler, and in the structure of ZB, (Figure 6) there is a hydrogen bonding. Therefore, the epoxy polymer composite EPIKOTE 1001 × 75/T31/ZB-5 has a better crosslinking density and the ZB filler creates more hydrogen bonding with the epoxy resin, so the T_g increases to 71 °C. ZB also plays the role of reducing the applied force, so the impact strength of the epoxy polymer film increases. The

T_g of epoxy polymer composite EPIKOTE 1001 × 75/T31/ZB-5/NS-1 increased to 82 °C because NS with the content of 1 wt % increased the bonding ability between ZB, the base resin, and the hardener. These results showed that the content of 1 wt % NS and 5 wt % ZB increased the toughness, impact strength, and mechanical properties of the epoxy polymer film EPIKOTE 1001 × 75/T31.

3.4.4. Thermal Behavior of the Epoxy Polymer Composite EPIKOTE 1001 × 75/T31/ZB/NS. The TG–DTG thermogravimetry analysis diagram of the epoxy polymer composite EPIKOTE 1001 × 75/T31/ZB-5/NS-1 is shown in Figure 11.

The TG–DTG curve from Figure 11 shows that the epoxy polymer composite EPIKOTE 1001 × 75/T31/ZB-5/NS-1 decomposes 5 wt % at the temperature range of 100–260 °C. The sample decomposes 20 wt % at 357 °C and decomposes 50 wt % at 403 °C. The sample has the strongest decomposition temperature at 380 °C with the decomposition rate of –15.49%/min.

The above results show that the starting decomposition temperature as well as the strongest decomposition temperature of epoxy polymer composite EPIKOTE 1001 × 75/T31 gradually increased from 363 to 370 °C (increased by 1.9%) with the content of 5 wt % ZB (sample EPIKOTE 1001 × 75/T31/ZB-5) and increased to 380 °C (increased by 4.7%) with the content of 5 wt % ZB and 1 wt % NS (sample EPIKOTE 1001 × 75/T31/ZB-5/NS-1).

These results show that NS and ZB increase the thermal stability of the epoxy polymer composite. The nanostructure that increases the thermal stability of nanocomposites is explained by the isolation and covering mechanisms. In nanocomposites, the polymer is surrounded by a large-surface-area nanoparticle. NS forms a protective layer for the underlying polymer material. NS plays a role in preventing the diffusion of oxygen required for polymer combustion. Besides, NS also plays the role of retaining heat and preventing the release of volatiles when the polymer burns. Therefore, the most important effect for nanocomposite materials to increase thermal stability and fire resistance is the ability of nanoparticles to cover and isolate.

Besides, ZB with a monocrystalline structure (Figure 6) reacts at high temperatures to form crosslinking, prevents smoke during combustion, reduces the formation of soot, and

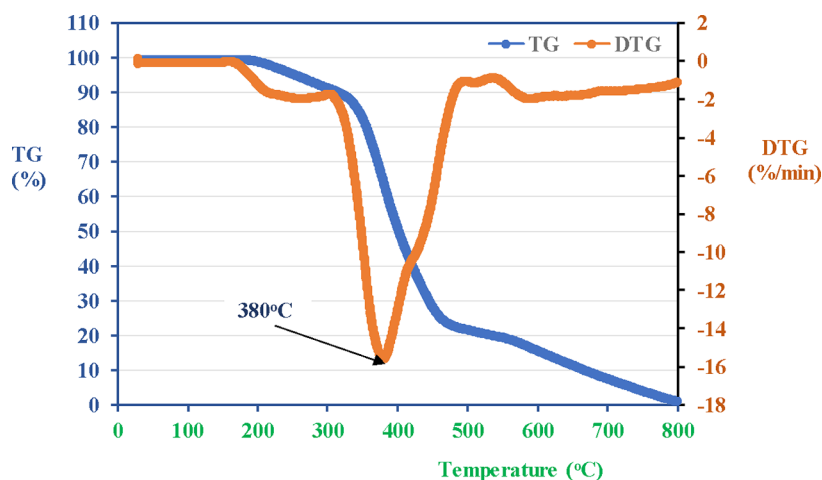


Figure 11. TG–DTG curve of epoxy polymer composite EPIKOTE 1001 × 75/T31/ZB-5/NS-1.

Table 5. Physical Chemistry and Mechanical Properties of Epoxy Coating Ep5ZBNS_C

| sample | dry film thickness (μm) | impact strength (kG cm) | flexibility (mm) | pencil hardness | adhesion | grinding fineness (μm) | viscosity (second) | dried time (h) | |
|-----------|--------------------------------------|-------------------------|------------------|-----------------|----------|-------------------------------------|--------------------|----------------|---------------|
| | | | | | | | | tack-free time | dry-hard time |
| Ep5ZBNS_C | 85.27 | 50 | 2 | 5H | 5B | 30 | 35 | 2 | 6 |

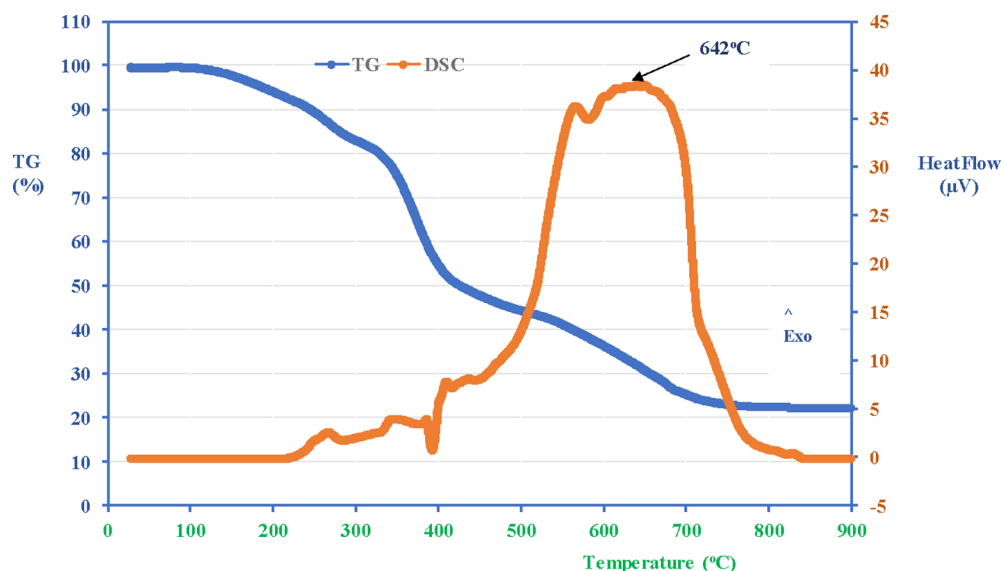


Figure 12. TG–DSC curve of epoxy coating Ep5ZBNS_C.

increases the thermal stability. In addition, hydrogen bonding in the structure of ZB also increases the thermal stability.^{15,29}

3.5. Effects of ZB and NS on the Mechanical Properties and Thermal Behavior of Epoxy Coating EPIKOTE 1001 \times 75/Hardener T31. Epoxy coating (sample Ep5ZBNS_C) is used for anticorrosion coating and in thermal equipment. Components of epoxy coating include part A and part B. Part A consists of epoxy resin EPIKOTE 1001 \times 75/ZB-5/NS-1 (with the content of 100 wt % epoxy resin EPIKOTE 1001 \times 75, 5 wt % ZB, and 1 wt % NS). The anticorrosion pigment system includes iron oxide (70 wt %), zinc chromate (60 wt %), and talc filler (20 wt %). Coating additives are dispersants, rheology agents, and plasticizers. The solvent system is used to adjust the volatility and viscosity for the coating as xylene/toluene/acetone (55:15:10, wt/wt/wt). Part B is a hardener T31.

Part A of epoxy coating Ep5ZBNS_C is made as follows: first, NS and ZB are dispersed in epoxy resin EPIKOTE 1001 \times 75 according to Section 3.5. Then, all the remaining ingredients are put into a ball mill and the mixture is ground for 6 h. The fineness of the epoxy paint reaches 30 μm .

Part B was mixed in part A with the content of 27 wt % hardener T31 in epoxy resin EPIKOTE 1001 \times 75. Some physical chemistry and mechanical properties of the epoxy coating are presented in Table 5.

The results in Table 5 show that the epoxy coating Ep5ZBNS_C is completely cured after 6 h. The impact strength of the coating film reaches 50 kG cm. The flexibility of coating film is 2 mm. The pencil hardness of the coating film reaches 5H. The adhesion of the coating film is 5B. The physical chemistry properties of the coating and the mechanical properties of the epoxy coating film Ep5ZBNS_C are both good for anticorrosion epoxy coating.³¹

The thermal properties of epoxy coating Ep5ZBNS_C were evaluated by TG–DSC thermal analysis, and the results are shown in Figure 12.

The results from the TG–DSC curve in Figure 12 are presented in Table 6.

Table 6. TG–DSC Thermal Analysis Results of Epoxy Coating Ep5ZBNS_C

| sample temperature ($^{\circ}\text{C}$) | TG lrsls (%) | heat flow l–bsls (μV) |
|---|--------------|------------------------------------|
| 29 | 100 | 0 |
| 194 | 95.00588 | 0 |
| 249 | 90.00326 | 1.781192 |
| 268 | 87.35124 | 2.736243 |
| 332 | 80.0072 | 2.848268 |
| 431 | 50.00434 | 8.044015 |
| 500 | 44.78206 | 13.01545 |
| 550 | 41.70011 | 32.29062 |
| 564 | 40.42013 | 36.24571 |
| 600 | 36.82542 | 37.36013 |
| 642 | 32.21959 | 38.58087 |
| 700 | 25.72738 | 30.41051 |

The TG–DSC curve in Figure 12 measures the change in thermal energy of the coating sample (heat flow, μV) and the percentage of the remaining coating sample mass (TG %) according to the decomposition temperature of the sample. The results from Figure 12 and Table 6 show that the starting decomposition temperature of epoxy coating Ep5ZBNS_C is about 193 $^{\circ}\text{C}$; this may be the evaporation process of the solvents. The epoxy coating sample decomposes 50 wt % at a temperature of 431 $^{\circ}\text{C}$. The maximum decomposition temperature (T_{max}) corresponds to the maximum thermal energy peak on the DSC curve at 642 $^{\circ}\text{C}$ (corresponding to a

Table 7. Thermal Behavior of Epoxy Polymer Composites and Coating Based on Epoxy Resin EPIKOTE 1001 × 75/T31^a

| sample | polymer | temperature °C | | | | |
|-----------|---------------------------------------|----------------|------------|------------|------------|-------------|
| | | $T_{5\%}$ | $T_{20\%}$ | $T_{50\%}$ | T_{\max} | DTG (%/min) |
| Ep0 | Epoxy EPIKOTE 1001 × 75/T31 | 197 | 337 | 380 | 363 | −8.49 |
| Ep5ZB | Epoxy EPIKOTE 1001 × 75/T31/ZB-5 | 260 | 352 | 388 | 370 | −9.15 |
| Ep5ZBNS | Epoxy EPIKOTE 1001 × 75/T31/ZB-5/NS-1 | 260 | 357 | 403 | 380 | −15.49 |
| Ep5ZBNS_C | Epoxy coating EPIKOTE 1001 × 75/T31 | 193 | 332 | 431 | 642 | −2.25 |

^a $T_{5\%}$, $T_{20\%}$, and $T_{50\%}$ —the rate of mass loss, T_{\max} —the strongest decomposition temperature DTG, (%/min)—decomposition rate.

heat flow of 38.58087 μV). The epoxy coating has a high decomposition temperature due to the presence of pigments and talc filler in the composition, and the epoxy coating is enhanced by ZB and NS. The ingredients in the coating form a protective layer to prevent oxygen from combustion, prevent the burning process, and increase thermal stability. The thermal behavior of epoxy polymer composites and coating based on epoxy resin EPIKOTE 1001 × 75/T31 is shown in Table 7.

The results of Table 7 show that the thermal properties of epoxy polymer composites and epoxy coatings gradually increase. The strongest T_{\max} gradually increased in the order of samples Ep0, Ep5ZB, Ep5ZBNS, and Ep5ZBNS_C, showing the role of hardener T31, ZB, and NS in increasing the thermal stability of the materials. The epoxy coating Ep5ZBNS_C has the high thermal stability due to its thermoset structure and is reinforced with fillers. In addition, ZB and NS form a protective layer that prevents oxygen from entering, limits the combustion process, and increases the thermal stability of the coating. The strongest decomposition temperature of epoxy coating Ep5ZBNS_C is 642 °C, showing that epoxy coating EPIKOTE 1001 × 75/T31/ZB-5/NS-1 has potential application in heat-resistant coatings.

4. CONCLUSIONS

In this study, the effects of hardener T31, ZB, and NS on the mechanical and thermal properties of epoxy composite materials were analyzed through efficiency analysis and evaluation methods. The results showed that the content of 5 wt % ZB and 1 wt % NS increased the mechanical properties, toughness, and thermal stability of epoxy polymer composite EPIKOTE 1001 × 75/T31, in which the epoxy polymer composite EPIKOTE 1001 × 75/T31/ZB-5/NS-1 is the best. The epoxy coating based on epoxy resin EPIKOTE 1001 × 75/T31/ZB-5/NS-1 with fillers, pigments, solvents, and additives has achieved the physical chemistry properties for anticorrosion coatings. Epoxy coating has the strongest decomposition temperature at 642 °C, showing potential application in heat-resistant coatings.

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Notes

The authors declare no competing financial interest.

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