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Effects of triphenyl phosphate (TPP) and nanosilica on the mechanical properties, thermal degradation of polymer nanocomposite materials and coating based on epoxy resin

Cuong Huynh Le Huy* ©, An Truong Thanh and Long Huynh Bao
Faculty of Chemical Engineering, Ho Chi Minh City University of Food Industry (HUFI), Ho Chi Minh City, VietNam
* Author to whom any correspondence should be addressed.
E-mail: cuonghlh@hufi.edu.vn, antt@hufi.edu.vn and longhb@hufi.edu.vn

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Abstract
Epoxi resin DER 671X75 cured with hardener T31. Epoxy polymer composite materials DER 671X75/T31 were improved the mechanical properties, thermal stability by triphenyl phosphate (TPP) and nanosilica (fumed silica S5505). Triphenyl phosphate and nanosilica were dispersed in epoxy resin DER 671X75 by mechanical stirring and ultrasonic vibration. The structural morphology of materials was characterized by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The thermal stability and thermal properties of materials were characterized by Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The results showed that triphenyl phosphate with a content of 5 wt% in epoxy resin DER 671X75 improved the mechanical properties of epoxy polymer coating film DER 671X75/T31 with an impact strength increased 25%. The contents of 5 wt% triphenyl phosphate and 1 wt% nanosilica in epoxy resin DER 671X75 improved the impact strength of epoxy polymer coating film DER 671X75/T31 by 125%. The thermal stability of epoxy nanocomposite materials DER 671X75/5% triphenyl phosphate/1% nanosilica/T31 increased 45.35%. Epoxy coatings based on epoxy resin DER 671X75/5% triphenyl phosphate/1% nanosilica/pigments/fillers/additives/hardener T31 achieved mechanical properties, physical chemistry properties for coating and, had thermal degradation over 500°C.

1. Introduction

Epoxy resins have been widely used for coatings, composites, adhesives, and molding materials due to their chemical resistance, good adhesion, and anti-corrosion [1]. However, because of many aromatic rings in chemical structure, epoxy resins are often hard and brittle. Flame resistance and thermal stability are other restrictions of epoxy resins [1–4]. To improve the disadvantages of epoxy resins, it can be done by modifying the main structure or replacing curing agents, or adding reinforcement additives [1, 5]. In recent years, one of the effective methods to increase the thermal stability of epoxy resins and polymers has been applied is the addition of flame retardants such as halogen compounds, antimony oxide, zinc borate, phosphorus compounds [2–21]. Improving the toughness of epoxy resins and polymer by nanocomposite structures has also been studied [22–28].

Halogen compounds are highly effective against fire, but often produce toxic products when burned, so their use is limited [6–8]. As a substitute for halogen compounds, phosphorus compounds show excellent heat resistance, exhibit high flame resistance, and are completely environmentally friendly [8–21]. Combustion of phosphorus compounds is low, has low toxicity, and forms a stable carbonization layer after burning [9–11]. The carbonization layer can prevent further pyrolysis of respective polymers, and also inhibits the use of the substance inside the product which is thermally decomposed into the gas phase [8]. Inorganic phosphorus flame retardants mainly refer to red phosphorus [12], ammonium polyphosphate (APP) [13]. Organic phosphorus flame retardants include phosphonates, phosphate esters, organic phosphorus salts, phosphorus heterocyclic...
compounds, triphenyl phosphate (TPP) [14–20]. Organic phosphorus flame retardants are one class of flame retardants with outstanding flame retardant properties for epoxy resin [19]. The main advantages of organic phosphorus flame retardants are low smoke emission, low toxicity, and environmental friendliness [8, 14–21].

In recent times, polymer composite materials with nanoparticles have been increasingly studied and applied [22–26]. Nanocomposite based on epoxy resin Epox 828 with 5–10 wt % nanosilica (Aerosil R974) increased UV resistance when formed film [22]. Modification of nanosilica by silane agents such as 3-aminopropl trimethoxy silane (KH-550), 3-glycidoxy propyl trimethoxy silane (KH-560) and 3-metacryloxypropyl trimethoxy silane (KH-570), used in synthesizing of poly (methyl methacrylate MMA–2-hydroxethyl methacrylate HEMA), increased surface activity [23]. Nanocomposite based on Bisphenol-A epoxy resin (Araldite® GY 6010) with 0–3 wt % nanosilica Aerosil R200 treated with γ-aminopropl trimethoxy silane (Amine A-100) increased mechanical properties and increased the glass transition temperature (Tg) according to the content of nanosilica [24]. Nanosilica (fumed silica S5505) with a content of 1 wt % increased the mechanical properties of nanocomposite materials based on epoxy resin DER 617X75 cured with Epicure 3125 [25]. Nanocomposite materials based on epoxy-silicon resin were reinforced with a content of 7 wt % nanoclay that increased the decomposition temperature for 60 wt % loss of clay reinforced Si-epoxy composites and improved mechanical properties with a content of 5 wt % clay reinforced Si-epoxy composites [26]. Nanocomposites based on phenol novolac epoxy resin were modified by unsaturated polyester resin and then reinforced using saosobit and silica nanoparticles at the different filler. Results showed that increasing the content of wt % silica nanoparticles could improve both thermal and mechanical properties, but increasing the content of more than 3 wt % silica nanoparticles could lead to a decrease in the mechanical properties [27]. Generally, the addition of nanomaterials in composite materials improved the mechanical properties, fracture toughness if the application type, suitable process, loadings, size, type of nanomaterials were implemented appropriately [28]. In the study [29], authors report a flame retardant epoxy nanocomposite reinforced with 9,10-dihydro-9-oxa-10-phosphaphenantrene-10-oxide (DOPO)- tethered SiO2 (DOPO-t-SiO2) hybrid nanoparticles (NPs). The DOPO-t-SiO2 NPs were successfully synthesized through surface treatment of SiO2 NPs with (3-glycidyloxypropyl)trimethoxysilane (GPTMS), followed by a click reaction between GPTMS on SiO2 and DOPO. The epoxy nanocomposites with DOPO-t-SiO2 NPs as multifunctional additive exhibited not only high flexural strength and fracture toughness but also excellent flame retardant properties and thermal stability.

Most previous studies have shown polymers were reinforced with suitable contents of weight nanoparticles that the mechanical properties of polymer composites were improved and flame retardant additives increased the thermal stability of polymer composite materials. In addition, there are currently no specific reports on studies using triphenyl phosphate (TPP) to increase the thermal stability of epoxy resins. Because of these studies, the combination of triphenyl phosphate (TPP) as a flame retardant and nanoparticles nanosilica to form nanocomposite based on epoxy resin has prospect to be more improvement of mechanical properties and thermal stability of polymer nanocomposite materials.

In this work, we focus on studying the effects of triphenyl phosphate (TPP) and nanosilica on the mechanical properties and thermal stability of the nanocomposite based on epoxy resin DER 671X75 cured with hardener T31 and its application in epoxy coating.

2. Materials and methods

2.1. Materials

Epoxy resin DER 671X75 (Bisphenol A diglycidyl ether (DGEBA)) with an epoxy equivalent weight (EEW) of 430–480 g /eq was purchased from Dow Chemicals. Hardener T31 (phenolic modified amine hardener) as epoxy resin curing agent with amine number of 450–550 mgKOH/g was purchased from Zhenjiang Danbao Resin (China). Nanosilica (S5505-Sigma). Triphenyl Phosphate (TPP) as phosphorus flame retardant (China). Pigments: Oxide Iron (China), Zinc Phosphate (France), Talc Filler (Taiwan). Crayvallac super (Arkema-France) as a rheology additive of high performance is suitable for a wide range of solvent-based, high-solids, and solvent-free applications. The plasticizer of Dioctyl Phthalate (DOP) (China). Troysperse CD1 (Thailand) is a general-purpose polymeric pigment dispersant and wetting additive for non-aqueous systems. Solvents: Xylene, Toluene, Acetone (China).

2.2. Preparation of polymer composite materials and coating film samples

2.2.1. Method of dispersing triphenyl phosphate into epoxy resin DER 671X75

Triphenyl phosphate with a content of 5 wt % to disperse in epoxy resin DER 671X75. Added 5.00 g of triphenyl phosphate (TPP) into 100.00 g of epoxy resin DER 671X75. All experimental chemicals were put in a 250 ml glass beaker and stirred at 500 rpm for 30 min, increased stirring speed to 1000 rpm for 60 min, continued to increase
stirring speed to 2000 rpm for 240 min. Investigating of the triphenyl phosphate contents in epoxy resin DER 671X75 was 3%, 5%, 7% by weight.

2.2.2. Method of dispersing nanosilica into epoxy resin DER 671X75
Dispersion of nanosilica with a content of 1 wt % according to the study \cite{25} that increased of mechanical properties polymer coating film based on epoxy resin DER 671X75/hardener Epicure 3125. Weigh 1.00 g of nanosilica S5505 into a 250 ml glass beaker. Added a certain amount of acetone solvent (5.00 g) to wet and swell nanosilica at a stirring speed of 200 rpm for 30 min. Then, added 100 g of epoxy resin DER 671X75 and increased the stirring speed to 2000 rpm for 30 min, followed by ultrasonic vibration for 50 min.

2.2.3. Method of dispersing nanosilica and triphenyl phosphate into epoxy resin DER 671X75
First, nanosilica S5505 (amount of 1.00 g) was dispersed into epoxy resin DER 671X75 (amount of 100.00 g) according to item 2.2.2 with a content of 1 wt %. Then, dispersed triphenyl phosphate (amount of 5.00 g) into the mixture of epoxy resin DER 671X75/1 wt % nanosilica according to the method in item 2.2.1.

2.2.4. Preparation of polymer composite materials samples for analysis
Epoxy polymer composite materials samples were cured with hardener T31. Dried samples at 110 °C for 2 h to cure completely. The samples were thinned about 50 μm for scanning SEM images. Completely cured samples were used for TG-DSC thermal analysis. The steel samples were prepared according to standards. The surface of samples was treated by mechanical methods of sanding, rinsing oil with acetone solvent, and dried at 100 °C for 1 h. Polymer coating film samples were coated on the treated steel by rolling method with the dry film thickness of 70–90 μm.

2.3. Analytical methods of polymer composite materials samples
Dispersion of triphenyl phosphate and nanosilica into epoxy resin DER 671X75 used the mechanical stirrer IKA-RW 20 (Germany) and ultrasonic device Sonics Vibram cell model CV334 (USA). The gel contents of polymer composite samples were determined by the method of extraction with acetone solvent in the Soxhlet set with a period of 10–12 h. TEM images were used for the evaluation of nanosilica dispersion in epoxy resin DER 671X75 by TEM Jeol model JEM 1400, Japan. Dispersion of triphenyl phosphate in epoxy resin DER 671X75 was determined by a scanning SEM image (SEM Jeol model JSM-IT 200, Japan). The thermal stability and thermal properties of polymer composite materials were characterized by TG-DSC on Setaram Labsys Evo (TG-DSC 1600 °C).

2.4. Standards for determination of mechanical properties of polymer coating films
The mechanical properties of polymer coating films are determined according to standards such as ISO, ASTM, and JIS. The flexibility of polymer coating films is determined according to standard ISO 1519:2002 (Erichsen, model 266). Coating films are bent through the shafts of metal cylinders with a diameter of 2–20 mm on the measuring instrument. The flexibility of coating films is expressed as the minimum diameter of the bending shaft which polymer coating films have not been damaged. The impact strength of coating films is determined according to standard ISO 6272:2002 (Erichsen, model 304) by using mechanical force to damage coating film. Impact strength of coating films is expressed as kG.cm which means that the maximum height (in cm) from which a load of mass 1 Kg falls freely on the specimen plate without causing damage to coating films. Adhesion of coating films is determined according to standard ASTM D3359-93 (Erichsen, model 295). Adhesion of coating films is determined based on the percentage of cells that are peeled off when coating films are cut into 1 mm × 1 mm cells and the adhesive tape is applied. The pencil hardness of coating films is determined by standard JIS K5400-90. The pencil hardness of polymer coating films is the hardness of the pencil in front of the pencil having a hardness that will scratch coating films. Dry film thickness is determined according to ASTM D1005 (Erichsen, model 296) or Vietnam National Standard TCVN 9406: 2012 (MiniTest 3100), using an electronic dry film thickness gauge with a magnetic induction probe for magnetic metal substrates such as iron and steel. Before measuring dry film thickness, the instrument needs to be calibrated on a standard membrane. Gently press and hold the probe until the instrument displays the measurement result (approximately 2 s to 3 s).
3. Results and discussion

3.1. Effects of triphenyl phosphate on the mechanical properties and thermal stability of epoxy polymer composite material DER 671X75/hardener T31

3.1.1. Dispersing of triphenyl phosphate into epoxy resin DER 671X75
The gel content of epoxy polymer composite material DER 671X75/hardener T31 was determined by the method of extraction with acetone solvent in Soxhlet set a period of 10–12 h. The results showed that the curing ratio between epoxy resin DER 671X75 and hardener T31 was 100: 30 (wt/wt) that obtained the highest gel content. Epoxy resin DER 671X75 and curing agent T31 achieved an optimal reaction ratio that reached the highest gel content. When the ratio between epoxy resin DER 671X75 and hardener T31 was not suitable, there would exist the non-reactive of epoxy resin DER 671X75 or T31 curing agent was residual, would be dissolved in acetone solvent, so the gel content was low. Thus, the highest gel content weight epoxy resin/hardener with curing ratio: epoxy resin DER 671X75/hardener T31 was 100: 30 (wt/wt) that was used for curing epoxy composite material samples. This result was similar to the study [25] when using hardener Epicure 3125 for curing epoxy resin DER 671X75.

The content of triphenyl phosphate is 5 wt % in epoxy resin DER 671X75 to investigate the method of dispersion. The SEM image of epoxy polymer composite material DER 671X75/5% triphenyl phosphate/T31 is shown in figure 1:

The SEM image from figure 1 shows that triphenyl phosphate is well dispersed in epoxy resin DER 671X75. Thus, the method of dispersing triphenyl phosphate into epoxy resin DER 671X75 by mechanical stirring is suitable. Figure 1 also shows that triphenyl phosphate crystals are evenly dispersed and separated on epoxy resin. So, the method of dispersion triphenyl phosphate by mechanical stirring is used to investigate the contents of triphenyl phosphate dispersing into epoxy resin DER 671X75.

3.1.2. Mechanical properties of epoxy polymer composite film DER 671X75/triphenyl phosphate/hardener T31
The contents of the investigation are 3, 5, 7 wt % triphenyl phosphate in epoxy resin DER 671X75. The mechanical properties of epoxy coating films DER 671X75/ triphenyl phosphate/T31 are shown in table 1.

The results from table 1 show that mechanical properties of polymer coating films such as flexibility, pencil hardness, adhesion are good to samples and there was almost no significant difference with the contents of 3, 5, 7 wt % triphenyl phosphate. The flexibility of coating film samples is all 2 mm, indicating that epoxy coating films have very good flexibility. To determine flexibility, coating films are bent through the shafts of metal cylinders with a diameter of 2–20 mm on the measuring instrument. The flexibility of coating films is expressed as the minimum diameter of the bending shaft which the polymer coating films have not been damaged (flaking, peeling, tearing, scratch, etc). The flexibility of coating films is 2 mm, which means that coating films are bent over a 2 mm diameter shaft without damaging coating films. The lower the test shaft diameter is, the better flexibility of coating films is.

Normally, when coating films are bent across the shaft, coating films often peel off with a low diameter shaft. The flexibility of coating films is related to the adhesion of coating films on the test steel substrate. The better adhesion of coating films is, the better flexibility of coating films is. To determine the adhesion of coating films on the steel substrate, cut 100 squares of 1 mm × 1 mm with a 1 mm slotted knife on coating films and apply adhesive tape to the 100 cells. Adhesion of coating films on the steel substrate is determined based on the
Table 1. Mechanical properties of epoxy coating films.

| Sample | Composition | Dry film thickness (µm) | Impact strength (kJ.cm) | Flexibility (mm) | Pencil hardness | Adhesion |
|--------|-------------|-------------------------|-------------------------|------------------|----------------|----------|
| E0     | Epoxy DER 671X75/T31 | 76.23                   | 20                      | 2                | 5H             | 5B       |
| E3TPP  | Epoxy DER 671X75/3% triphenyl phosphate/T31 | 78.9                    | 20                      | 2                | 4H             | 5B       |
| E5TPP  | Epoxy DER 671X75/5% triphenyl phosphate/T31 | 83.38                   | 25                      | 2                | 5H             | 5B       |
| E7TPP  | Epoxy DER 671X75/7% triphenyl phosphate/T31 | 75.15                   | 22.5                    | 2                | 3H             | 5B       |
percentage of cells that are peeled off the steel substrate when the adhesive tape is removed. Adhesion 5B means that when the adhesive tape is removed, 0% of the cells are peeled off from the steel substrate, the adhesion of the coating film is very well. If the amount of cells peeled off is less than 5%, the adhesion is 4B (according to ASTM D 3359-97). The pencil hardness of coating films is determined based on the hardness of the pencil tip causing scratches on the coating films. The pencil hardness of coating films is 5H which means using a pencil with a hardness of 5H will not scratch the coating film, but a pencil with a hardness of 6H will cause scratches to the coating film. Impact strength of coating films is determined by using a load of mass 1 kilogram (kg), raising to a specified height (cm) from low to high, falling freely, impacting the coating film and causing damage to the coating film (ASTM ISO 6272:2002, Erichsen, model 304). The value of the impact strength is determined at the highest position of the load without causing damage to the coating film. The impact strength of the coating film is 20 kG.cm which means that the maximum height of 20 cm from which a load of mass 1 kG falls freely on the specimen plate without causing damage to the coating film. The impact strength of coatings films depends on the brittleness of coating films. Due to many aromatic rings in chemical structure, epoxy resins are brittle [1]. Epoxy resin DER 617X75 has many aromatic rings in chemical structure and hardener T31 as phenolic modified amine hardener in which there are many aromatic rings. So, epoxy polymer composite DER 617X75/hardener T31 has more aromatic rings, epoxy coating films are brittle and the impact strength of epoxy coating film DER 617X75/T31 is only 20 kG.cm. Adding content of 5 wt % triphenyl phosphate (sample E5TPP), epoxy coating film DER 617X75/5% triphenyl phosphate/T31 improve impact strength from 20 kG.cm to 25 kG.cm (increased 25%). Triphenyl phosphate has also acted as a reinforced filler for epoxy polymer, epoxy resin is a substrate polymer that binding triphenyl phosphate fillers, the optimum ratio between fillers and matrix polymer improve the mechanical properties of polymer composite. The mechanical properties of epoxy coating film DER 617X75/T31 are the best with the E5TPP sample (the content of 5 wt % triphenyl phosphate). The content of 3 wt % triphenyl phosphate in epoxy resin DER 617X75, properties of epoxy polymer composite DER 617X75/3% triphenyl phosphate/T31 show the properties of epoxy resin DER 617X5 due to the low content of weight triphenyl phosphate filler. The content of 7 wt % triphenyl phosphate, the content of weight epoxy resin DER 617X75 is not enough to cover and bond triphenyl phosphate filler and thus, properties of epoxy composite DER 617X75/7% triphenyl phosphate/T31 show the properties of triphenyl phosphate, that the reason for low mechanical properties of epoxy coating films.

3.1.3. Thermal stability of epoxy polymer composite material DER 617X75/triphenyl phosphate/hardener T31
The TG-DSC thermal analysis diagram of epoxy polymer composite material DER 617X75/hardener T31 is shown in figure 2:

The TG-DSC thermal analysis results of epoxy polymer composite material DER 617X75/T31 are presented in table 2:

The results from the TG-DSC thermal analysis diagram in figure 2 and table 2 show that the starting temperature decomposition of epoxy polymer composite DER 617X75/T31 is about 150 °C–158 °C. In this temperature range, the decomposition is mainly due to the evaporation of solvents. The strongest decomposition temperature of the sample corresponds to the peak with the largest energy on the DSC curve (HeatFlow 1.204957 μV) at 339.96 °C. The percentage of residual mass at 500 °C is 16.52%. The chemical structure and
composition of epoxy resin DER 671X75 and the modified phenolic T31 curing agent have many aromatic rings, so epoxy polymer composite material DER 671X75/T31 has high thermal stability. Epoxy polymer composite material DER 671X75/T31 is a cross-linked thermosetting resin structure. The chemical structure and cross-linking density of epoxy polymer composite DER 671X75/T31 are the factors that make up thermal stability [25].

On the DSC from figure 2, the glass transition temperature Tg is about 190 °C due to the high cross-linking density and many aromatic rings in the epoxy composite structure DER 671X75/T31. The Tg marks a polymer’s transition from an amorphous glass to a rubbery solid and defines the limits of processability for most polymer. The peak at 69.22 °C represents the loss of the volatile component which acetone solvent is used to adjust the viscosity of epoxy resin DER 671X75 curing with T31. The process of solvent evaporation in the sample continues to occur up to a temperature of 150 °C–158 °C. The epoxy polymer sample DER 671X75/T31 is completely cured 100% at the peak of 234 °C on the DSC curve. On the DSC curve, there are also other peaks at 374.11 °C, 484.61 °C, and 618.13 °C, which also show that the thermal decomposition of the sample continues or can be the instability of the DSC’s baseline.

The TG-DSC thermal analysis diagram of epoxy composite polymer material DER 671X75/5% triphenyl phosphate/T31 is shown in figure 3:

The TG-DSC thermal analysis results of epoxy polymer composite material DER 671X75/T31 are presented in table 3:

The results from the TG-DSC thermal analysis diagram in figure 3 and table 3 show that the starting decomposition temperature of epoxy polymer DER 671X75/5% triphenyl phosphate/T31 is about 158 °C–187 °C. The strongest decomposition temperature corresponds to the peak with the largest energy on the DSC curve at 345.07 °C (HeatFlow 2.222902 μV). The percentage of residual mass at 500 °C is 28.29%.

The results from figures 2, 3, tables 2 and 3 show that the thermal stability of epoxy polymer composite material DER 671X75/5% triphenyl phosphate/T31 is better than epoxy polymer composite material DER 671X75/T31, with the highest decomposition temperature increases from 339.96 °C to 345.07 °C. Thus,
Triphenyl phosphate with a content of 5 wt % increases the thermal stability of the epoxy polymer DER 671X75/T31. Triphenyl phosphate has the following chemical formula (Figure 4).

Triphenyl phosphate (TPP) with chemical formula is shown in Figure 4 that consists of three aromatic rings around the phosphate group. The aromatic rings in triphenyl phosphate are chemically resistant to thermal stability. So, triphenyl phosphate is enhanced for the epoxy polymer composite DER 671X75/T31, the thermal stability of epoxy composite material DER 671X75/triphenyl phosphate/T31 is better. According to the study [21], triphenyl phosphate was completely decomposed with the heat starting at around 200°C. The mechanism of heat stability, fire resistance of triphenyl phosphate mainly took place in the gas phase, under the effect of temperature, triphenyl phosphate would decompose to create free radicals $PO\cdot$, $PO_2\cdot$, and was able to capture free radicals $H\cdot$, $OH\cdot$, generated in the combustion process, thereby reducing the number of active centers that affected on the development of combustion of the material. Triphenyl phosphate also contributed to the solid-phase fire resistance mechanism. In the thermal decomposition process, triphenyl phosphate could form a protective thin solid layer covering the surface of the material, which played the role of preventing the release of the products produced in the polymer degradation process and preventing diffusion of oxygen into the burning zone [30, 31].

### Table 3. TG-DSC thermal analysis results of epoxy polymer composite material DER 671X75/5% triphenyl phosphate/T31.

| Sample Temperature (°C) | TG (\%) | HeatFlow | Heat | bs (\(\mu\)V) |
|-------------------------|---------|-----------|------|----------------|
| 31.52888                | 100     | 0         | -0.59279 |
| 64.93263                | 100.0023| -0.13386  |
| 158.4032                | 98.93986| -0.15318  |
| 160.915                 | 98.2471 | -0.00223  |
| 200.0152                | 97.92179| 0.238481  |
| 345.0716                | 86.05397| 2.222902  |
| 375.5703                | 68.58176| -3.16443  |
| 430.5829                | 39.04512| -31.3822  |
| 500.0577                | 28.2967 | -1.24224  |

Figure 4. Chemical formula of triphenyl phosphate (TPP).

3.2. Effects of nanosilica and triphenyl phosphate on the mechanical properties, thermal stability of epoxy polymer composite DER 671X75/nanosilica/triphenyl phosphate/hardener T31

3.2.1. Mechanical properties of epoxy polymer composite coating film DER 671X75/nano silica/triphenyl phosphate/T31

Nanosica (fumed silica S5505) with a content of 1 wt % is dispersed in epoxy resin DER 671X75. The TEM image of epoxy nanocomposite material DER 671X75/1% nanosilica/T31 is shown in Figure 5:
The TEM image from figure 5 shows that nanosilica (fumed silica S5505) is well dispersed in epoxy resin DER 671X75 to form a nanocomposite structure. Nanosilica particles are dispersed into epoxy resin DER 671X75. However, nanosilica particles tend to combine, there are regions of the nanosilica particles with an average size of about 10–20 nanometers. These result are similar to other studies [23, 25, 32]. Due to the high surface activity is formed by the bonds of the Si–O group, adjacent nanosilica particles tend to gather and cluster together to form larger size particles.

The mechanical properties of epoxy coating films DER 671X75/1% nanosilica/5% triphenyl phosphate/T31 are presented in table 4:

The TG-DSC thermal analysis results of epoxy polymer composite material DER 671X75/1% nanosilica/5% triphenyl phosphate/T31 are presented in table 5:

Table 5. TG-DSC thermal analysis results of epoxy polymer composite material DER 671X75/1% nanosilica/5% triphenyl phosphate/T31.

The TEM image from figure 5 shows that nanosilica (fumed silica S5505) is well dispersed in epoxy resin DER 671X75/T31 to form a nanocomposite structure. Nanosilica particles are dispersed into epoxy resin DER 671X75. However, nanosilica particles tend to combine, there are regions of the nanosilica particles with an average size of about 10–20 nanometers. These result are similar to other studies [23, 25, 32]. Due to the high surface activity is formed by the bonds of the Si–O group, adjacent nanosilica particles tend to gather and cluster together to form larger size particles.

The mechanical properties of epoxy coating films DER 671X75/1% nanosilica/5% triphenyl phosphate/T31 are presented in table 4:

The results from table 4 show that the mechanical properties of epoxy coating film DER 671X75/1% nanosilica/5% triphenyl phosphate/T31 significantly increase the impact strength of polymer coating film from 20 kG.cm to 45 kG.cm (increased by 125%). According to the study [25], the content of 1 wt % nanosilica also increased the mechanical properties of epoxy coating film DER 671X75/Epicure 3215. It can be seen that nanosilica with a content of 1 wt % improves compatibility triphenyl phosphate with epoxy resin DER 671X75 and nanoparticles nanosilica with a characteristic of nano size and high surface activity that increases the interoperability with epoxy resin, thereby the toughness of epoxy polymer coating film DER 671X75/1% nanosilica/5% triphenyl phosphate/T31 (E5TPPSi sample) is improved.

3.2.2. Thermal stability of epoxy polymer composite material DER 671X75/tri phenyl phosphate/nanosilica/hardener T31

The TG-DSC thermal analysis diagram of epoxy polymer composite material DER 671X75/1% nano silica/5% triphenyl phosphate/T31 (E5TPPSi sample) is shown in figure 6:

The TG-DSC thermal analysis results of epoxy polymer composite material DER 671X75/1% nanosilica/5% triphenyl phosphate/T31 are presented in table 5:

The TG-DSC thermal analysis results from figure 6 and table 5 show that the starting temperature decomposition of epoxy polymer composite material DER 671X75/1% nanosilica/5% triphenyl phosphate/
T31 is about 210 °C–214 °C. The strongest decomposition temperature corresponds to the peak with the largest energy on the DSC curve at the temperature of 494.12 °C (HeatFlow 2.386507 μV). The percentage of residual mass at 500 °C is 19.34%.

The above results show that the thermal stability of the epoxy polymer composite material DER 671X75/T31 in ascending order is E0, E5TPP, E5TPPSi samples. The starting of decomposition temperature, as well as the strongest decomposition temperature of epoxy polymer DER 671X75/T31 gradually increases from 339.96 °C (E0 sample), increases to 345.07 °C (the content of 5 wt % triphenyl phosphate, E5TPP sample), and increases to 494.12 °C (up 45.35%, content of 5 wt % triphenyl phosphate and 1 wt % nanosilica, E5TPPSi sample). Nanosilica with a content of 1 wt % increased thermal stability of the epoxy composite polymer material DER 671X75/Epicure 3125 [25]. Nanocomposite/nanosilica increases the thermal stability because polymer molecules encapsulate with nanosilica particles and nanosilica particles act to prevent the diffusion of oxygen necessary for polymer combustion. In addition, nanosilica particles also play a role in keeping heat and hindering the release of volatile products when the polymer burns. So, the combination of triphenyl phosphate and nanosilica in nanocomposite material significantly increases the thermal stability of epoxy polymer composite material DER 671X75/T31.

### 3.3. Effects of nanosilica and triphenyl phosphate on the mechanical properties, thermal stability of epoxy coating

The coating based on epoxy resin DER 671X75 (PE5TPPSi) is manufactured with the composition in table 6. The components in the PE5ZBSi epoxy coating in table 6 include epoxy resin DER 671X75, triphenyl phosphate, nanosilica, pigments, fillers, additives, solvents, and hardener T31. Epoxy paint is used to protect anti-corrosion for steel structures and heat equipment, so in the paint composition used filler pigment system with corrosion resistance and heat resistance. In which, the composition of iron oxide pigment, talc filler,

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#### Table 5. TG-DSC thermal analysis results of epoxy polymer composite material DER761X75/1% nanosilica/5% triphenyl phosphate/T31.

| Sample temperature (°C) | TG | HeatFlow | HeatFlow | HeatFlow |
|--------------------------|----|----------|----------|----------|
|                          |   |          |          |          |
| 28.07195                 | 100| 0        |          |          |
| 69.17218                 | 100.0009| −0.4038 |          |          |
| 210.0228                 | 99.03637| 0.442051|          |          |
| 214.1854                 | 99.00013| 0.504626|          |          |
| 297.5617                 | 98.37627| −0.90426|          |          |
| 312.2277                 | 98.00222| −0.47729|          |          |
| 494.1214                 | 19.56637| 2.386507|          |          |
| 500.0061                 | 19.34543| 2.184209|          |          |
| 600.0153                 | 16.83253| 0.273688|          |          |
pigment inhibited zinc phosphate corrosion process similar to research results of the study [33]. Other components in the PESZBSi epoxy coating include Troyperse CD1 as a general-purpose polymeric pigment dispersant and wetting additive for non-aqueous systems. Crayvallac super is a high performance, micronized amide wax rheology modifier suitable for a wide range of solvent-based, high-solids, and solvent-free applications. The plasticizer of dioctyl phthalate (DOP) improves the toughness and flexibility of epoxy coating films. Nanosilica (fumed silica S5505) reinforces the mechanical properties, anti-corrosion, and increases thermal stability for paint [25, 32, 33]. Triphenyl phosphate (TPP) enhances the mechanical properties and thermal stability of epoxy coating films. A mixture of solvents is xylene, toluene, acetone for adjusting viscosity, volatility, and drying time of the coating film. Curing for epoxy coating uses a T31 curing agent according to the ratio of epoxy resin DER 671X75/hardener T31: 100/30 (wt/wt).

Some physical chemistry properties of epoxy coating DER 671X75 and mechanical properties of the coating are presented in table 7:

The epoxy coating DER 671X75/T31 has the composition of iron oxide pigment system, zinc phosphate, talc filler, and other components according to table 6. Epoxy paint is milled in a ball mill for 8 h to reach the grinding fineness of 25 μm. The measured results in table 7 show that epoxy coating DER 671X75/T31 obtains all the necessary properties for steel protection coating.

The TG-DSC thermal analysis diagram of epoxy coating DER 671X75 is shown in figure 7:

The TG-DSC thermal analysis results of epoxy coating DER 671X75 are presented in table 8:

The results from figure 7 and table 8 show that the starting temperature decomposition of epoxy coating DER 671X75/T31 (PE5TPPSi) is about 210 °C–249 °C. The strongest decomposition temperature of the paint sample corresponds to the peak with the largest energy on the DSC curve is 524.31 °C (HeatFlow 6.810669 μV).

The percentage of residual mass at 500 °C is 58.06%. The thermal stability of the PE5TPPSi epoxy coating due to chemical structure and composition of epoxy based on resin DER 671X75/curing agent phenolic modified amine T31, the paint is enhanced by iron oxide pigment system, talc filler, zinc phosphate corrosion inhibiting pigment, nanosilica, and triphenyl phosphate. The components in the PE5TPPSi epoxy coating have the effect of thermal stability, also increase anti-corrosion of the coating.

### Table 6. Epoxy coating composition.

| Epoxy coating | Composition | Weight (%) |
|---------------|-------------|------------|
| Part A        | Epoxy resin DER 671X75 | 100        |
|               | Nanosilica (fumed silica S 5505) | 1.0        |
|               | Iron oxide | 75         |
|               | Zinc phosphate | 60         |
|               | Talc filler | 15         |
|               | Troyperse CD1 | 1.5        |
|               | Plastilizer dioctylphthalate (DOP) | 8          |
|               | Crayvallac super | 1          |
|               | Triphenyl phosphate (TPP) | 5          |
|               | Xylene | 52.5       |
|               | Toluene | 15         |
|               | Acetone | 7.5        |
| Part B        | Hardener T31 | 30         |

### Table 7. Mechanical properties of epoxy coating film and epoxy coating DER 671X75/T31.

| Sample     | Dry film thickness (μm) | Impact strength (kg.cm) | Flexibility (mm) | Pencil hardness | Adhesion | Grinding fineness (μm) | Viscosity (second) | Tack-free time | Dry-hard time |
|------------|-------------------------|--------------------------|------------------|----------------|----------|------------------------|-------------------|----------------|---------------|
| PE5TPPSi   | 88.35                   | 50                       | 2                | SH             | 5B       | 25                     | 32                | 2              | 6             |
The thermal degradation of epoxy polymer composite materials DER 671X75/T31 and epoxy coating DER 671X75/T31 are summarized and presented in Table 9:

The results from Table 9 show that polymer composite materials and epoxy coating based on epoxy resin DER 671X75/T31 have high thermal stability. The thermal stability of samples increases gradually in the order of samples E0, E5TPP, E5TPPSi, PE5TPPSi. In particular, epoxy nanocomposite materials DER 671X75 reinforce with the content of 1 wt % nanosilica and content of 5 wt % triphenyl phosphate, the thermal stability increases significantly with the strongest decomposition temperature increases from 339.96 °C to 494.12 °C (increased 45.35%) and epoxy coating PE5TPPSi is 524.31 °C (increased 54.23%) that indicating potential application for high thermal resistant epoxy paints above 500 °C.

### 4. Conclusions

The mechanical properties of the epoxy polymer composite film DER 671X75/hardener T31 increased with a content of 5 wt % triphenyl phosphate, the impact strength increased from 20 kG.cm to 25 kG.cm (increased 25%). The impact strength of epoxy polymer composite coating film DER 671X75/5% triphenyl phosphate/1% nanosilica/T31 increased from 20 kG.cm to 45 kG.cm (increased 125%). The thermal stability of epoxy polymer composite material increased according to the order of epoxy DER 671X75/T31, epoxy DER 671X75/5% triphenyl phosphate/T31, epoxy DER 671X75/1% nanosilica/5% triphenyl phosphate/T31. The thermal stability of epoxy nanocomposite material DER 671X75/1% nanosilica/5% triphenyl phosphate/T31 increased by 45.35%. The epoxy coating based on epoxy resin DER 671X75/T31 was reinforced with a content of 1 wt % nanosilica, 5 wt % triphenyl phosphate and pigments, additives achieved mechanical properties, physical chemistry properties for coating, and had thermal degradation over 500 °C.

### Table 8. TG-DSC thermal analysis results of epoxy coating DER 671X75.

| Sample Temperature (°C) | TG [%] | HeatFlow [-]s | HeatFlow [-]μV |
|-------------------------|--------|---------------|---------------|
| 29.18078                | 100    | 0             | -0.00254      |
| 174.3705                | 99.271 | 0.081425      | 1.76631       |
| 189.2832                | 98.7956| 1.406016      | 3.976011      |
| 200.0064                | 94.2396| 1.767974      | 6.810669      |
| 249.4915                | 83.2747| 2.852022      | 5.618408      |
| 319.2277                | 62.8672| 5.618408      | 2.852022      |
| 362.5306                | 53.4042| 6.180669      | 2.852022      |
Table 9. Thermal degradation of epoxy polymer composite materials DER 671X75/T31.

| Sample  | Composition                                           | The starting decomposition temperature (°C) | The strongest decomposition temperature (°C) | Percentage of residual mass at 500 °C (%) |
|---------|-------------------------------------------------------|---------------------------------------------|---------------------------------------------|------------------------------------------|
| E0      | Epoxy DER 671X75/T31                                  | 150–158                                     | 339.96                                     | 16.52                                     |
| ESTPP   | Epoxy DER 671X75/5% triphenyl phosphate/T31           | 158–187                                     | 345.07                                     | 28.29                                     |
| ESTPPSi | Epoxy DER 671X75/5% triphenyl phosphate/1% nanosilica/T31 | 210–214                                     | 494.12                                     | 19.34                                     |
| PESTPPSi| Epoxy coating DER 671X75/5% triphenyl phosphate/1% nanosilica/pigments/fillers/T31 | 210–249                                     | 524.31                                     | 56.86                                     |
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Cuong Huynh Le Huy 🅰https://orcid.org/0000-0002-8015-7678

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