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Effects of Phosphorus Compounds, Montmorillonite Clay on the Thermo-Mechanical Properties of Epoxy Resins and Their Coatings

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Abstract

This study investigates the effects of triphenyl phosphate (TPP) and montmorillonite (MMT) clay on the thermo-mechanical properties of epoxy nanocomposites and coatings based on Kukdo YD-011X75 epoxy resin cured with G-5022. TPP and MMT were dispersed into the epoxy resin using mechanical stirring combined with ultrasonic treatment. The morphology and dispersion state were characterized by SEM, XRD, and TEM, while thermal behavior was evaluated using TGA and DTG. The results confirmed uniform clay dispersion and partial exfoliation within the epoxy matrix. The incorporation of 4 wt.% TPP and 1 wt.% MMT individually increased the impact strength by 61.8% and 47.1%, respectively. A pronounced synergistic effect was observed for the combined system, yielding an impact strength of 100 KG·cm (194.1% higher than neat epoxy). The optimized coating exhibited enhanced thermal stability and is promising for heat-resistant protective coating applications.

Highlights

- Exfoliated MMT clay was successfully dispersed in Kukdo YD-011X75/G-5022 epoxy resin.
- The combination of 4 wt.% TPP and 1 wt.% clay increased impact strength by 194.1%.
- The modified epoxy coating exhibited high thermal stability with 47.54 wt.% residue at 500°C.

1. INTRODUCTION

Epoxy resins are among the most widely used thermosetting polymers because of their excellent adhesion, high mechanical strength, chemical resistance, electrical insulation, and thermal stability. Consequently, epoxy materials have been extensively applied in coatings, adhesives, electronic encapsulation, and fiber-reinforced composites [1]. However, conventional epoxy resins exhibit inherent brittleness and relatively poor flame resistance, which limit their use in applications requiring high thermal stability and fire safety [1, 2].

In recent decades, polymer nanocomposites have attracted considerable attention because nanoscale fillers can significantly improve the mechanical, thermal, and multifunctional properties of polymer matrices at relatively low loading levels [3]. Among various nanofillers, montmorillonite (MMT) clay has been widely investigated owing to its layered structure, large specific surface area, and ability to create tortuous diffusion pathways that restrict heat and mass transfer during thermal degradation [4–6].

The use of phosphorus-containing flame retardants has become an important strategy for improving the fire performance of polymeric materials. Patrick [2] reported that ammonium polyphosphate (APP) significantly improved the flame retardancy of epoxy/glass fiber composites while maintaining the glass transition temperature. Early studies demonstrated that phosphorus compounds promote char formation and reduce heat release during combustion [8–11]. Wu et al. [12] and Liu et al. [13] further showed that phosphorus-based systems effectively enhance thermal stability through condensed-phase char formation mechanisms. Reviews by van der Veen and de Boer [9], Hörold [10], and Levchik [17]

highlighted the high efficiency of halogen-free phosphorus flame retardants and their increasing industrial importance because of environmental and health concerns associated with halogenated flame retardants.

Besides phosphorus additives, nanoclay has been extensively incorporated into epoxy systems to improve mechanical and thermal properties. Manfredi et al. [4] demonstrated that the incorporation of montmorillonite into glass fiber/epoxy composites enhanced mechanical performance owing to the formation of intercalated clay structures. Khalili et al. [6] reported that the addition of 1 wt% nanoclay increased the tensile strength of epoxy adhesive joints, whereas 3 wt% nanoclay produced the highest impact resistance. Muralishwara et al. [14] reviewed epoxy–clay nanocomposite coatings and concluded that approximately 1 wt% nanoclay often provides the optimum balance between dispersion and performance, while excessive loading may lead to agglomeration and property deterioration. Similar observations were reported in polyurethane systems, where nanoclay improved thermal stability and flame retardancy at moderate loading levels [15]. Nanotechnology-based fillers have also been widely recognized as effective modifiers for advanced protective coatings [16].

The combination of phosphorus flame retardants and nanoclay has been investigated as a promising route to achieve synergistic improvements in thermal and fire performance. Hussain and Varley [18] demonstrated that both organo-phosphorus compounds and nanoclay individually improved the thermal stability and flame retardancy of epoxy resins. Charalampos et al. [5] further reported that phosphorus flame retardants combined with modified nanoclay significantly reduced the peak heat release rate and improved the fire safety of glass-fiber-reinforced epoxy composites. Recent reviews have emphasized that phosphorus-containing flame retardants remain among the most effective and environmentally friendly approaches for flame-retardant epoxy thermosets [19, 21, 28, 31].

Achieving uniform nanoclay dispersion remains a major challenge in epoxy nanocomposites. Chun et al. [20] demonstrated that ultrasonic treatment effectively reduced nanoclay agglomeration and improved the dispersion quality of clay platelets in epoxy matrices, resulting in enhanced mechanical properties. Therefore, ultrasonic dispersion has become one of the most widely adopted techniques for fabricating epoxy/clay nanocomposites.

Previous studies have also explored the incorporation of phosphorus-containing additives and nanoparticles into epoxy systems. Cuong et al. [7] reported that the simultaneous addition of 5 wt.% triphenyl phosphate (TPP) and 1.0 wt.% nanosilica increased the impact strength of epoxy coatings by approximately 125% and improved thermal stability by more than 45%. In another study, Cuong et al. [22] found that nano silica improved the thermal stability and corrosion resistance of epoxy coatings reinforced with micaceous iron oxide (MIO). Similarly, Cuong et al. [27] demonstrated that a combination of zinc borate and nano silica increased the glass transition temperature from 52°C to 82°C and enhanced the thermal stability of epoxy nanocomposites.

Numerous studies on flame-retardant polymer systems have reported significant synergistic effects between phosphorus compounds and inorganic additives. Fang et al. [23] showed that APP and

expandable graphite (EG) produced a strong synergistic effect in polylactide, resulting in a limiting oxygen index (LOI) of 36.5% and a UL-94 V-0 rating. Wang et al. [24] reported that intumescent flame-retardant polyethylene systems exhibited improved thermal stability and lower heat release rates. Similar synergistic effects of APP and EG were observed in poly(butylene terephthalate) composites [25]. Xian et al. [26] and Wei et al. [29] demonstrated that the incorporation of phosphorus flame retardants and nanostructured additives significantly improved the flame-retardant behavior and thermal stability of rigid polyurethane foams. These findings suggest that combining phosphorus-containing compounds with nanoscale inorganic fillers can effectively enhance thermal degradation resistance and flame retardancy through barrier and char-forming mechanisms.

Recent advances in phosphorus-based flame retardants have focused on multifunctional systems containing phosphorus, nitrogen, and silicon. Fang et al. [30, 35] synthesized a novel phosphorus/nitrogen/silicon flame retardant for epoxy resin and reported a substantial increase in char yield together with a reduction in heat release and smoke production. Reviews by Indresh and Akella [28] and Siqi and Pingan [19] concluded that phosphorus-containing flame retardants represent one of the most promising directions for next-generation flame-retardant epoxy materials. Zheng et al. [36] developed a hyperbranched phosphorus-containing flame retardant for epoxy resins and demonstrated significant improvements in char formation and thermal degradation resistance. Additional studies on phosphorus-containing polymer/clay nanocomposites have further confirmed the effectiveness of phosphorus-based flame-retardant systems in enhancing thermal stability [32].

More recently, nanoclay-reinforced epoxy composites have attracted renewed attention. Shahrajabian et al. [33] reported that the incorporation of 5 wt% nanoclay increased the tensile strength of epoxy/glass fiber/TiC–TiB_2 composites from 116 MPa to 223 MPa and reduced the wear rate from 3.7 to 0.4 mg/Nm. Shahrajabian and Vaezzadeh [34] showed that the addition of 3 phr nanoclay improved tensile strength by approximately 10%, flexural strength by 9.2%, and flame retardancy by about 41% in epoxy/glass fiber/ATH hybrid composites. These studies clearly demonstrate the potential of nanoclay for simultaneously enhancing the mechanical, thermal, and flame-retardant properties of epoxy-based materials.

Recent studies have further confirmed the effectiveness of combining phosphorus-based flame retardants and nanoclay fillers in epoxy systems. Dai et al. [37] developed a phosphorus–silicon synergistic reactive flame retardant (PTSi) that simultaneously enhanced flame retardancy and mechanical performance. With only 2 wt% PTSi, the limiting oxygen index (LOI) increased from 22.6% to 28.5% and achieved UL-94 V-0 classification, while tensile strength and impact strength improved by 11.2% and 86.3%, respectively. Su et al. [38] reported that 5 wt% functionalized montmorillonites increased the storage modulus by approximately 44%, while also improving thermal stability, glass transition temperature, and moisture resistance. Miturska and Rudawska [39] demonstrated that incorporating 3 wt% MMT into epoxy coatings increased tensile and flexural strengths by up to 15% and 20%, respectively, and significantly enhanced coating adhesion and durability. Altaf et al. [40] synthesized organoclay-based flame-retardant epoxy nanocomposites and observed a 28–34% increase in char yield

together with UL-94 V-0 flame-retardant performance owing to the synergistic action of organoclay and aluminum trihydroxide. Similarly, Örçen and Bayram [41] found that the addition of 1 wt% nanoclay increased the tensile strength of glass-fiber-reinforced epoxy composites by 31.06%, while also improving stiffness and glass transition temperature. These recent findings highlight the growing interest in exploiting synergistic interactions between phosphorus-containing flame retardants and layered silicate nanofillers to simultaneously improve flame resistance, thermal stability, and mechanical properties of epoxy materials.

Despite extensive research on phosphorus flame retardants and nanoclay-reinforced epoxy systems, limited studies have systematically investigated the combined effects of triphenyl phosphate (TPP), montmorillonite clay, and curing agents on the thermo-mechanical behavior of epoxy coatings. In particular, the synergistic influence of TPP and nanoclay dispersed by ultrasonic treatment in epoxy resin Kukdo YD-011X75 cured with Kukdo G-5022 has not been comprehensively evaluated.

Therefore, the present work aims to investigate the effects of TPP, montmorillonite clay, and the curing agent Kukdo G-5022 on the mechanical properties, thermal behavior, and thermal degradation resistance of epoxy nanocomposites and coatings based on Kukdo YD-011X75 epoxy resin. The novelty of this study lies in the systematic evaluation of the synergistic interactions between a phosphorus-containing additive and nanoclay in a commercial epoxy coating system, together with the correlation between filler dispersion, mechanical performance, and thermal stability.

2. RESULTS AND DISCUSSION

2.1. Curing Ratio of Kukdo YD-011X75 Epoxy Resin with Kukdo G-5022 Curing Agent

The stoichiometric curing ratio of the Kukdo YD-011X75 epoxy resin and Kukdo G-5022 polyamide curing agent was calculated based on the relationship between the Epoxy Equivalent Weight (EEW) of the resin and the Amine Hydrogen Equivalent Weight (AHEW) of the curing agent. The Kukdo G-5022 hardener has an AHEW ranging from 165 to 185 g/eq, with an average value of 175 g/eq, while the Kukdo YD-011X75 epoxy resin exhibits an EEW of 450–500 g/eq, with an average value of 475 g/eq. Accordingly, the stoichiometric amount of curing agent was determined from the AHEW/EEW ratio (175/475), corresponding to a curing agent-to-epoxy resin ratio of 0.37 (wt/wt). Therefore, 37 parts by weight of G-5022 curing agent were used per 100 parts by weight of YD-011X75 epoxy resin to ensure complete curing and optimal crosslinking of the epoxy network.

The curing process involves a chemical reaction between the active hydrogen atoms of the polyamide and the epoxide functional groups of the resin. This reaction facilitates crosslinking, resulting in a thermoset polymer network. The general reaction mechanism is illustrated in Fig. 1.

As illustrated in Fig. 1, the curing reaction between Kukdo YD-011X75 epoxy resin and Kukdo G-5022 polyamide hardener results in the formation of a crosslinked thermoset network. The formulation was prepared by thoroughly mixing 100 parts by weight of epoxy resin with 37 parts by weight of curing agent, corresponding to the calculated stoichiometric ratio based on the Amine Hydrogen Equivalent Weight (AHEW) and Epoxy Equivalent Weight (EEW).

Initial curing was performed at ambient temperature for 6 hours, followed by a post-curing phase at 60°C for 60 minutes to ensure complete crosslinking and structural stabilization. The gel content of the cured system was determined to be approximately 90%, as measured by acetone solvent extraction [2, 22, 27]. These results are consistent with methodologies and findings reported in previous studies [7, 22, 27]. Miturska and Rudawska [39] demonstrated that the type of curing agent strongly affects the performance of epoxy systems, with polyamide-cured epoxy exhibiting superior mechanical strength and adhesion compared to amine-cured epoxy.

The obtained results are consistent with previous studies demonstrating that both curing chemistry and nanoparticle incorporation strongly influence the final performance of epoxy systems. In our earlier studies, epoxy systems cured with T31 hardener and modified with TPP, nano silica, zinc borate, or micaceous iron oxide exhibited significant improvements in toughness, thermal stability, and coating performance [7, 22, 27]. The enhanced properties were attributed to the formation of a well-developed crosslinked network together with the homogeneous dispersion of nano-sized fillers within the epoxy matrix.

The present study further confirms the importance of curing efficiency, as the cured epoxy system exhibited a gel content of approximately 90%, indicating a high degree of crosslinking. Similar observations were reported by Miturska and Rudawska [39], who found that the curing agent type significantly affected the mechanical and adhesion properties of epoxy coatings. Epoxy systems cured with polyamide hardeners exhibited superior mechanical performance compared with amine-cured systems, highlighting the critical role of curing chemistry in determining network structure and final material properties.

Compared with previous epoxy systems containing nano silica, zinc borate, TPP, and MIO (micaceous iron oxide) [7, 22, 27], the incorporation of clay in the current work provides an additional reinforcement mechanism through its layered structure and high aspect ratio. The combination of effective curing, high gel content, and uniform clay dispersion is expected to enhance interfacial interactions and restrict polymer chain mobility, thereby contributing to improved thermal and mechanical performance of the epoxy nanocomposites.

2.2. Mechanical Properties of Epoxy Polymer Composites and Epoxy Paint Based on Kukdo YD-011X75/G-5022

Effect of TPP on the Mechanical of Epoxy Polymer Composites

Dispersion of TPP into Epoxy Resin

A content of 4 wt.% triphenyl phosphate (TPP) was employed to study its dispersion within the Kukdo YD-011X75 epoxy matrix. The dispersion was achieved through a dual technique involving mechanical stirring followed by ultrasonic vibration. The epoxy/TPP mixture was subsequently cured using a weight ratio of 100:37 (epoxy resin to Kukdo G-5022 hardener). The microstructure of the cured composite containing 4 wt.% TPP was analyzed via scanning electron microscopy (SEM), as illustrated in Fig. 2.

The SEM micrograph presented in Fig. 2 reveals a relatively homogeneous distribution of triphenyl phosphate (TPP) throughout the Kukdo YD-011X75 epoxy matrix cured with Kukdo G-5022 hardener. The absence of large agglomerates and phase-separated domains indicates good compatibility between TPP and the epoxy system, which is essential for achieving uniform stress distribution under mechanical loading. A homogeneous dispersion of TPP minimizes stress concentration sites and promotes efficient load transfer from the epoxy matrix to the dispersed phase, thereby contributing to enhanced mechanical performance.

The microstructure also suggests that the curing reaction between the epoxy resin and G-5022 hardener was sufficiently effective to immobilize and stabilize the TPP particles within the crosslinked network. The high gel content (approximately 90%) obtained for the cured system further supports the formation of a dense three-dimensional network capable of restricting particle migration and phase segregation during curing. Such a network structure is expected to improve dimensional stability and maintain the integrity of the filler–matrix interface during thermal and mechanical loading.

Interestingly, the TPP particles exhibit irregular morphology, surface defects, and internal porous features. These microstructural characteristics can play an important role in toughening mechanisms. The porous structure may increase the effective interfacial area between TPP and the epoxy matrix, promoting stronger physical interlocking and interfacial adhesion. Moreover, under external stress, pores and defects can act as sites for localized plastic deformation, crack deflection, crack pinning, and energy dissipation. Instead of propagating directly through the matrix, cracks may be forced to deviate around TPP domains, thereby increasing the fracture path length and the energy required for crack growth.

From a thermal perspective, the uniform distribution of TPP is also advantageous because TPP acts as a phosphorus-containing flame-retardant additive. Well-dispersed TPP can facilitate the formation of a more homogeneous protective char layer during thermal degradation, reducing heat transfer and slowing the decomposition process. Therefore, the observed microstructure is expected to contribute not only to improved toughness but also to enhanced thermal stability and flame-retardant performance.

The present observations are consistent with our previous study [7], in which TPP was successfully dispersed in DER 671X75 epoxy resin cured with T31 hardener. However, the current epoxy Kukdo YD-011X75 /G-5022 system appears to provide similarly effective dispersion despite differences in resin and curing chemistry, suggesting that the reinforcing and flame-retardant effects of TPP are not solely dependent on the filler itself but are also strongly influenced by the structure and crosslink density of the

cured epoxy network. These findings further support the conclusion that achieving a uniform TPP dispersion and strong filler–matrix interactions is critical for maximizing the mechanical and thermal performance of epoxy-based composite materials.

Effect of TPP on the Mechanical Properties of Epoxy Polymer Films Based on Kukdo YD-011X75/TPP/G-5022

Triphenyl phosphate (TPP) was added to Kukdo YD-011X75 epoxy resin at loadings of 2, 4, and 6 wt.% to assess its effect on the mechanical properties of the cured coatings. The epoxy coatings were formulated using Kukdo YD-011X75 epoxy resin and Kukdo G-5022 curing agent, and their mechanical properties were subsequently evaluated. The results presented in Table 1 indicate that the addition of TPP significantly affects the mechanical behavior of the epoxy coatings, reflecting changes in the microstructure and filler–matrix interactions within the cured epoxy network.

Table 1
Mechanical properties of epoxy polymer composite films and epoxy paint based on Kukdo YD-011X75/G-5022

Sample	Polymer Epoxy	Thickness (µm)	Adhesion	Flexibility (mm)	Pencil hardness	Impact strength (KG.cm)
EP	Kukdo YD-011X75/G-5022	129.95	5B	4	6H	34
EP-TPP2	Kukdo YD-011X75/2%TPP/G-5022	97.9	5B	2	4H	50
EP-TPP4	Kukdo YD-011X75/4%TPP/G-5022	103.3	5B	2	4H	55
EP-TPP6	Kukdo YD-011X75/6%TPP/G-5022	117.5	5B	2	5H	52.5
EP-Clay_1	Kukdo YD-011X75/1%Clay/ G-5022	94.2	5B	2	4H	50
EP-Clay_2.5	Kukdo YD-011X75/2.5%Clay/ G-5022	106.1	4B	2	5H	47.5
EP-Clay_3	Kukdo YD-011X75/3%Clay/ G-5022	112.6	3B	2	5H	45
EP-TPP4-Clay_1	Epoxy YD-11X75/4 wt.%TPP/ 1 wt.% Clay/G-5022	82.85	5B	2	5H	100
EP paint	Epoxy YD-11X75/4 wt.%TPP/ 1 wt.% Clay/G-5022, fillers, pigments, additives, solvents	165.6	5B	2	5H	69

As shown in Fig. 1, the cured Kukdo YD-011X75/G-5022 epoxy system possesses a highly crosslinked three-dimensional network containing a large number of aromatic rings. Although such a molecular architecture provides excellent hardness, adhesion, and chemical resistance, it also restricts polymer chain mobility, resulting in inherent brittleness and relatively low impact resistance [1, 2, 7, 9].

Consequently, the unmodified epoxy coating (EP) exhibited an impact strength of only 34 KG.cm and a flexibility value of 4 mm, indicating limited resistance to sudden mechanical deformation.

For practical protective coating applications, epoxy coatings are generally required to exhibit an impact strength greater than 50 KG.cm and a flexibility value of 2 mm or lower in order to withstand mechanical stress without cracking [7, 22, 27]. Therefore, improving the toughness of the epoxy network while maintaining its intrinsic hardness and adhesion remains an important challenge. In the present study, triphenyl phosphate (TPP) was introduced as a functional additive to modify the microstructure of the cured epoxy system and enhance its mechanical performance.

The results summarized in Table 1 demonstrate that the incorporation of TPP significantly improves the mechanical behavior of the epoxy coatings. All TPP-containing formulations (EP-TPP2, EP-TPP4, and EP-TPP6) exhibited a flexibility value of 2 mm, compared with 4 mm for the unmodified epoxy coating. This remarkable improvement indicates that TPP effectively increases the ability of the coating to accommodate deformation without crack initiation. The enhancement can be attributed to the ability of dispersed TPP domains to redistribute local stresses and reduce stress concentration within the highly crosslinked epoxy network. Furthermore, the porous and defect-containing morphology of TPP particles observed by SEM may contribute to energy dissipation during deformation, thereby delaying crack propagation and improving coating toughness.

The adhesion performance remained unchanged after TPP incorporation, with all formulations achieving the highest classification (5B). This result indicates that the addition of TPP does not adversely affect the interfacial interactions between the epoxy coating and the substrate. The excellent adhesion can be attributed primarily to the strong chemical bonding and crosslinked structure generated during curing of the Kukdo YD-011X75 epoxy resin with the G-5022 hardener. Similar observations have been reported in previous studies involving epoxy systems modified with TPP, nano silica, zinc borate, and micaceous iron oxide, where the incorporation of functional fillers improved toughness and thermal stability without compromising coating adhesion [7, 22, 27].

The pencil hardness results reveal a slight decrease in surface hardness with increasing TPP content. This behavior is expected because improvements in flexibility and toughness are often accompanied by a modest reduction in rigidity. Nevertheless, all formulations maintained acceptable hardness values, indicating that the beneficial toughening effect of TPP was achieved without significant deterioration of the coating surface properties.

Among all investigated formulations, EP-TPP4 exhibited the highest impact strength, reaching 55 KG.cm, corresponding to an increase of 61.8% compared with the unmodified epoxy coating. The EP-TPP2 and EP-TPP6 formulations also showed substantial improvements, reaching 50 KG.cm and 52.5 KG.cm, respectively. These results clearly demonstrate that TPP acts as an effective toughening agent in the Kukdo YD-011X75/G-5022 epoxy system.

The observed dependence of impact strength on TPP content suggests the existence of an optimum filler concentration. At low loading (2 wt.%), the amount of dispersed TPP is insufficient to effectively modify the fracture behavior of the epoxy network. The mechanical response therefore remains largely governed by the brittle epoxy matrix, resulting in a lower impact strength than that achieved at higher TPP concentrations. In contrast, when the TPP content increases to 6 wt.%, the probability of particle-particle interactions and local agglomeration increases. Excessive filler content may reduce the continuity of the epoxy matrix and create microstructural heterogeneities that act as crack initiation sites under impact loading. Consequently, the reinforcing efficiency decreases despite the higher TPP concentration.

At 4 wt.% TPP, an optimal balance between filler content and matrix continuity appears to be achieved. The TPP particles are sufficiently abundant to promote stress redistribution and energy absorption while remaining uniformly dispersed throughout the epoxy matrix. This microstructural configuration maximizes interfacial interactions and minimizes defect formation, resulting in the highest impact strength and overall mechanical performance. The SEM observations support this interpretation by revealing a homogeneous distribution of TPP within the epoxy matrix.

The present findings are in good agreement with our previous studies on TPP-modified epoxy systems [7], where the incorporation of 5 wt.% TPP into DER 671X75/T31 epoxy increased impact strength by approximately 25%. However, the current Kukdo YD-011X75/G-5022 system achieved a 61.8% increase at only 4 wt.% TPP, suggesting a more efficient toughening effect. This difference may be attributed to variations in epoxy chemistry, curing agent structure, crosslink density, and filler-matrix interactions. Furthermore, previous studies involving zinc borate/nano silica [27] and MIO/nano silica [22] demonstrated that improvements in epoxy performance are strongly dependent on filler dispersion and interfacial compatibility. The current results indicate that TPP alone can provide a significant toughening effect without the need for additional nanofillers.

The role of curing chemistry should also be considered. Miturska and Rudawska [39] reported that the type of curing agent significantly influences the mechanical performance of epoxy systems, with polyamide-cured coatings exhibiting superior toughness and adhesion compared with amine-cured systems. Similarly, the favorable mechanical properties observed in the present work suggest that the Kukdo G-5022 curing agent contributes to the formation of a well-balanced crosslinked network capable of effectively interacting with dispersed TPP particles. Therefore, the mechanical enhancement observed in the epoxy/TPP coatings can be attributed not only to the presence of TPP but also to the synergistic effect between TPP dispersion and the cured epoxy network structure.

Overall, the results demonstrate that TPP is an effective toughening additive for Kukdo YD-011X75/G-5022 epoxy coatings. An optimum TPP content of 4 wt.% provides the best balance between flexibility, adhesion, hardness, and impact resistance, resulting in a coating system that satisfies the mechanical requirements for high-performance protective applications.

Effect of Clay on the Mechanical Properties of Epoxy Polymer Composites

Dispersion of Clay into Kukdo YD-011X75 Epoxy Resin

To improve the nanostructure of the epoxy composite, 1.0 wt.% clay was dispersed into Kukdo YD-011X75 epoxy resin through combined mechanical stirring and ultrasonic vibration. The resulting clay morphology and degree of dispersion within the epoxy matrix were characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM).

The XRD patterns of the pristine clay and the epoxy/clay nanocomposite are shown in Fig. 3. These characterization techniques were employed to determine the structural evolution of the clay galleries after incorporation into the epoxy matrix and to evaluate whether intercalated or exfoliated nanostructures were formed. The obtained results provide important information regarding filler–matrix interactions and the effectiveness of the clay dispersion process.

The XRD spectral results of the Kukdo YD-011X75/1.0 wt.% clay epoxy composite and the pure clay powder (Fig. 3) reveal characteristic diffraction peaks corresponding to the layered structure of the clay. Specifically, the YD-011X75/1.0 wt.% clay composite sample shows a diffraction peak at 2θ = 18.476° (θ = 9.238°), whereas the clay powder sample shows characteristic peaks at 2θ = 26.476° (θ = 13.373°) and 2θ = 29.537° (θ = 14.769°).

Using the Bragg equation ($n\lambda = 2d \cdot \sin\theta$), with an assumed first-order diffraction (n = 1) and an X-ray wavelength of λ = 1.540560 Å, the interlayer spacing (d_{001}) of the clay can be calculated. The calculated values of d_{001} for the respective samples are summarized in Table 2.

Table 2
XRD measurement results of Kukdo YD-011X75/1 wt.% clay and clay epoxy samples

Sample	**Epoxy polymer**	**2θ (º)**	**Basal spacing (d_{001}), Å**	**Nanocomposite structure**
Clay	Clay	26.476	33.34	-
		29.537	30.44	
EP-Clay_1	Kukdo YD-011X75/ 1%clay/G-5022	18.476	49.039	Exfoliated nanocomposite

As shown in Table 2, the pristine clay exhibited basal spacings (d_{001}) of 33.34 Å and 30.44 Å at 2θ values of 26.476° and 29.537°, respectively. After incorporation into the Kukdo YD-011X75 epoxy matrix, the characteristic diffraction peak shifted toward a lower diffraction angle (2θ = 18.476°), corresponding to an increased basal spacing of 49.04 Å. The substantial expansion of the interlayer galleries indicates that epoxy chains successfully penetrated between the clay layers during processing. Such an increase in d-spacing suggests the formation of a highly intercalated nanostructure and provides strong evidence of effective clay dispersion within the epoxy matrix. The pronounced gallery expansion also implies partial exfoliation of clay platelets, which is expected to enhance filler–matrix interactions and facilitate

the development of a nanocomposite structure with improved mechanical and thermal properties [38, 40, 41].

The significant increase in basal spacing observed after incorporation of clay into the epoxy matrix indicates that epoxy chains successfully penetrated the clay galleries, resulting in extensive expansion of the layered silicate structure. This structural evolution suggests the formation of a highly intercalated morphology and, in some regions, partial to predominant exfoliation of clay platelets within the epoxy matrix. Similar increases in gallery spacing have been reported for epoxy/montmorillonite nanocomposites and are generally considered evidence of effective filler dispersion and strong filler–matrix interactions [3–6, 38, 40].

The improved dispersion can be attributed to the combined effect of mechanical stirring and ultrasonic treatment employed during composite preparation. One of the major challenges in fabricating clay-based nanocomposites is the strong tendency of clay platelets to aggregate due to interparticle van der Waals attractions. The application of ultrasonic vibration generates cavitation-induced microjets and localized shear forces that facilitate the delamination of clay tactoids and suppress agglomeration. Consequently, individual clay layers become more readily accessible to epoxy molecules, promoting polymer intercalation and the formation of nanostructured morphologies.

The development of intercalated and exfoliated structures is particularly beneficial because it significantly increases the interfacial area between the clay platelets and the epoxy matrix. The resulting nanoscale dispersion enhances stress transfer efficiency and creates a tortuous pathway for heat and mass transport through the material. Similar observations have been reported by Su et al. [38], who demonstrated that improved montmorillonite dispersion enhanced the thermal and mechanical performance of epoxy nanocomposites. Likewise, Altaf et al. [40] reported that increased clay gallery spacing facilitated the formation of well-dispersed epoxy nanocomposites and contributed to improved thermal stability and char formation.

Therefore, the XRD results confirm that the adopted dispersion process effectively disrupted the original clay stacking structure and promoted the formation of a nanocomposite architecture with enhanced filler–matrix interaction, which is expected to contribute positively to the mechanical and thermal properties of the cured epoxy system.

TEM image of Kukdo YD-011X75/1 wt.% Clay/G-5022 epoxy composite is shown in Fig. 4.

The TEM micrograph of the Kukdo YD-011X75/clay nanocomposite is presented in Fig. 4. The image clearly reveals the presence of well-dispersed clay platelets distributed throughout the epoxy matrix. Individual silicate layers and small stacks of separated platelets can be observed, indicating that extensive delamination of the original clay occurred during processing. These observations confirm the formation of a predominantly exfoliated nanocomposite structure [3–6, 14–16, 20–21, 38, 40, 41].

The exfoliated morphology observed by TEM is in good agreement with the XRD results, which showed a substantial increase in basal spacing following clay incorporation into the epoxy resin. The combined XRD and TEM analyses therefore demonstrate that the clay layers were successfully separated and dispersed at the nanoscale within the crosslinked epoxy network. Such a morphology is generally regarded as the most desirable structure for polymer/clay nanocomposites because it maximizes the interfacial contact area between the silicate layers and the polymer matrix.

The formation of an exfoliated nanostructure can be attributed to the synergistic effect of mechanical stirring and ultrasonic treatment. Ultrasonic cavitation promotes the breakup of clay agglomerates and facilitates the delamination of layered silicates, thereby enabling more effective penetration of epoxy chains between adjacent clay layers. As a result, homogeneous nanoscale dispersion of the clay platelets is achieved throughout the epoxy matrix.

The high aspect ratio and large specific surface area of the exfoliated clay nanosheets are expected to enhance filler–matrix interactions and improve the efficiency of stress transfer within the composite. Furthermore, the dispersed silicate layers create a tortuous diffusion pathway that can restrict the transport of heat, oxygen, and volatile degradation products through the polymer matrix. Similar exfoliated morphologies and their associated reinforcing effects have been reported for montmorillonite/epoxy nanocomposites by Su et al. [38], Altaf et al. [40], and Örçen and Bayram [41]. Therefore, the TEM observations provide direct evidence that the adopted processing method successfully produced a predominantly exfoliated epoxy/clay nanocomposite with favorable structural characteristics for property enhancement.

Effect of Clay on the Mechanical Properties of Epoxy Polymer Films Based on Kukdo YD-011X75/TPP/G-5022

The mechanical properties of Kukdo YD-011X75/G-5022 epoxy composites containing different clay loadings (1.0, 2.5, and 3.0 wt.%) were evaluated, and the results are presented in Table 1. The addition of clay is expected to influence the mechanical behavior of the epoxy matrix through changes in filler dispersion, interfacial interactions, and nanocomposite morphology. Therefore, flexibility, impact strength, adhesion, and pencil hardness were systematically examined to assess the reinforcing effect of clay and to determine the optimum clay content for maximizing composite performance.

The mechanical performance data summarized in Table 1 indicate that the incorporation of clay significantly influences the behavior of the Kukdo YD-011X75/G-5022 epoxy system. The flexibility of all clay-reinforced epoxy films remained at 2 mm, demonstrating that the addition of clay up to 3 wt.% did not adversely affect the ductility of the coating. In contrast, a slight reduction in pencil hardness and adhesion was observed with increasing clay content. This behavior may be attributed to the introduction of inorganic clay platelets into the epoxy matrix, which can locally interfere with the continuity of the crosslinked network and reduce the effective contact area between the coating and substrate when excessive filler is present.

A more pronounced effect was observed for impact strength. All clay-containing samples exhibited higher impact resistance than the neat epoxy film, confirming the reinforcing effect of nanoclay. Among the investigated formulations, EP-Clay_1 exhibited the highest impact strength (50 KG.cm), corresponding to a 47% improvement compared with the unmodified epoxy system. Further increases in clay loading to 2.5 wt.% and 3 wt.% resulted in impact strengths of 47.5 and 45 KG.cm, respectively. Although these values remained higher than that of the neat epoxy, the gradual decline in impact strength suggests that excessive clay loading reduced the reinforcing efficiency of the nanofiller [15–16, 20–21].

The improved impact strength observed at 1 wt.% clay can be attributed to the predominantly exfoliated nanostructure confirmed by XRD and TEM analyses. The homogeneous dispersion of high-aspect-ratio clay nanosheets provides a large interfacial area between the filler and epoxy matrix, enabling efficient stress transfer and hindering crack initiation and propagation during impact loading. The dispersed clay layers can act as barriers that deflect growing cracks, absorb fracture energy, and promote crack branching, thereby increasing the toughness of the epoxy network. Similar toughening mechanisms have been reported for montmorillonite/epoxy nanocomposites by Su et al. [38] and Örçen and Bayram [41], who observed simultaneous improvements in mechanical performance and thermal stability when clay was uniformly dispersed at relatively low loadings.

The reduction in impact strength at clay contents above 1 wt.% is likely associated with the increased probability of particle aggregation and incomplete exfoliation. As filler concentration increases, interparticle interactions become stronger, making homogeneous dispersion more difficult to maintain. Localized agglomerates may act as stress concentration sites that facilitate crack initiation and reduce the effectiveness of load transfer between the epoxy matrix and clay platelets. Similar observations were reported by Miturska and Rudawska [39], who demonstrated that the mechanical performance of epoxy coatings depends not only on clay content but also on the quality of filler dispersion and the resulting network structure. Likewise, Altaf et al. [40] reported that the beneficial effects of nanoclay are maximized when sufficient exfoliation and interfacial interaction are achieved.

Overall, the results indicate that 1 wt.% clay represents the optimum loading for the Kukdo YD-011X75/G-5022 epoxy system. At this concentration, the clay platelets are effectively exfoliated and uniformly distributed within the epoxy matrix, maximizing stress-transfer efficiency and crack-deflection mechanisms while minimizing filler agglomeration. Consequently, the EP-Clay_1 formulation provides the most favorable balance between toughness, flexibility, and overall mechanical performance

Combined Effects of Triphenyl Phosphate and Nano Clay on the Mechanical and Thermal Properties of Kukdo YD-011X75/G-5022 Epoxy Polymer Films

Mechanical Properties of Epoxy Polymer Films Reinforced with 4 wt.% Triphenyl Phosphate and 1 wt.% Clay

The preceding results demonstrated that the incorporation of either 4 wt.% triphenyl phosphate (TPP) or 1 wt.% nanoclay individually improved the mechanical and thermal performance of the Kukdo YD-011X75/G-5022 epoxy system. Based on these findings, a hybrid formulation containing both 4 wt.% TPP and 1 wt.% nanoclay was developed to investigate the potential synergistic effects of combining the two reinforcing additives.

The mechanical properties of the epoxy coating film based on Kukdo YD-011X75 epoxy resin, G-5022 curing agent, 4 wt.% TPP, and 1 wt.% nanoclay are summarized in Table 1. This formulation was designed to integrate the toughening and char-forming capability of TPP with the reinforcing and barrier effects of exfoliated clay nanosheets. The combined incorporation of these additives is expected to promote enhanced filler–matrix interactions, improve stress-transfer efficiency, and increase resistance to thermal degradation, thereby producing an epoxy coating with superior mechanical performance and thermal stability compared with systems containing either additive alone.

The mechanical performance results presented in Table 1 confirm that the epoxy composite film formulated with Kukdo YD-011X75, 4 wt.% TPP, and 1 wt.% clay (EP-TPP4-Clay_1) exhibits the most significant enhancement among all tested samples, particularly in terms of impact strength. The impact strength reached 100 KG.cm, representing a 194% increase compared to the unmodified epoxy film (EP).

This substantial improvement is attributed to the synergistic interaction between TPP and clay, which function as reinforcing fillers within the epoxy matrix. Similar synergistic effects have been reported in systems combining nano-silica and TPP [7]. The combined presence of TPP and clay enhances interfacial bonding with the epoxy resin (Kukdo YD-011X75), resulting in a composite material with superior mechanical integrity [7, 14–16, 20, 22].

The remarkable increase in impact strength suggests that the toughening mechanisms associated with TPP and clay operate in a complementary manner. TPP contributes to reducing the inherent brittleness of the highly crosslinked epoxy network by facilitating energy dissipation during deformation, whereas the exfoliated clay nanosheets act as effective reinforcing elements that improve stress transfer and inhibit crack initiation and propagation. Consequently, the EP-TPP4-Clay_1 composite benefits from multiple toughening mechanisms, including crack deflection, crack pinning, interfacial stress redistribution, and localized energy absorption, resulting in significantly enhanced impact resistance.

The effectiveness of the clay reinforcement is strongly related to the exfoliated nanostructure confirmed by the XRD and TEM analyses. The homogeneous dispersion of clay nanosheets provides a large interfacial area for interaction with the epoxy matrix, thereby maximizing load-transfer efficiency and reinforcing the polymer network. Similar observations have been reported by Su et al. [38], who demonstrated that well-dispersed functionalized montmorillonite improved the stiffness, thermal stability, and overall performance of epoxy nanocomposites. Likewise, Örçen and Bayram [41] reported that epoxy composites containing 1 wt.% nanoclay exhibited the most favorable mechanical properties, whereas higher clay loadings resulted in reduced effectiveness due to particle aggregation. The

optimum performance observed for the EP-Clay_1 formulation in the present study is therefore consistent with the literature.

The present results also agree with the findings of Miturska and Rudawska [39], who reported that montmorillonite can significantly improve the mechanical performance of epoxy coatings when appropriate filler dispersion and curing conditions are achieved. Their study showed that the reinforcing efficiency of clay depends not only on filler concentration but also on the quality of filler–matrix interactions and the resulting network structure. In the current work, the excellent dispersion achieved through mechanical stirring combined with ultrasonic treatment appears to have maximized the reinforcing contribution of the clay nanosheets.

In addition, Altaf et al. [40] demonstrated that organoclay-modified epoxy nanocomposites exhibited improved structural integrity and thermal resistance owing to enhanced interfacial interactions between the clay layers and the epoxy matrix. Although their study focused primarily on flame-retardant performance, the observed improvements in composite morphology and filler dispersion support the mechanical enhancement mechanism proposed in the present work.

Compared with the epoxy systems containing only 4 wt.% TPP (EP-TPP4) or only 1 wt.% clay (EP-Clay_1), the EP-TPP4-Clay_1 formulation exhibits a substantially greater improvement in impact strength than would be expected from the individual contributions of each additive alone. This finding provides strong evidence of a synergistic effect between the phosphorus-containing modifier and the exfoliated clay nanosheets. The combined reinforcement mechanism enables the epoxy network to simultaneously achieve improved toughness, efficient stress transfer, and resistance to crack propagation, thereby producing a composite coating with superior mechanical performance.

Importantly, the exceptional increase in impact strength was achieved while maintaining excellent adhesion (5B), high flexibility (2 mm), and satisfactory hardness (4H). Such a balanced property profile is highly desirable for protective coating applications, where coatings are required to withstand both mechanical loading and service-induced deformation without failure. Therefore, the EP-TPP4-Clay_1 formulation satisfies the performance requirements for advanced epoxy coating systems [22] and represents a promising approach for developing multifunctional epoxy nanocomposite coatings with enhanced mechanical durability and thermal stability.

Effect of TPP and Clay on Mechanical Properties of Kukdo YD-011X75/G-5022 epoxy paint

The epoxy paint formulation was designed as a two-component system consisting of Part A and Part B. Part A comprised Kukdo YD-011X75 epoxy resin (100 parts by weight), nanoclay (1 part), triphenyl phosphate (TPP, 4 parts), talc filler (5 parts), iron oxide pigment (75 parts), zinc phosphate anticorrosive pigment (60 parts), solvent (75 parts), Bentone Bengel 908 rheological additive (0.5 part), and SilTech C1700 wetting/dispersing additive (0.5 part). Part B consisted of the G-5022 curing agent.

Part A was prepared by dispersing and grinding all solid components in a ball mill for 6 h until a fineness of approximately 25 μm was achieved. Prior to application, Part B was mixed with Part A at a resin-to-curing-agent ratio of 100:37 (wt/wt), corresponding to the stoichiometric formulation of the Kukdo YD-011X75/G-5022 epoxy system.

In this formulation, the epoxy resin served as the primary film-forming binder, providing adhesion and cohesion within the coating matrix. Iron oxide and zinc phosphate functioned as pigments and anticorrosive agents, while talc acted as an extender filler to improve coating uniformity and mechanical integrity. The solvent and additives facilitated pigment dispersion, rheological control, and processing characteristics. Nanoclay and TPP were incorporated as functional reinforcing additives to enhance the mechanical performance and thermal stability of the coating through nanoscale reinforcement and phosphorus-assisted stabilization mechanisms, respectively.

Mechanical and Thermal Properties of Kukdo YD-011X75/4 wt.% TPP/1 wt.% Clay/G-5022 Epoxy Paint

The mechanical properties of the epoxy paint formulated with Kukdo YD-011X75 epoxy resin, 4 wt.% TPP, 1 wt.% clay, and G-5022 curing agent are summarized in Table 1.

The mechanical properties summarized in Table 1 demonstrate that the epoxy paint formulated with Kukdo YD-011X75 epoxy resin, 4 wt.% TPP, 1 wt.% clay, and G-5022 curing agent exhibits a balanced combination of mechanical strength, adhesion, flexibility, and curing performance. The coating achieved an impact strength of 69 KG.cm, adhesion rating of 5B, flexibility of 2 mm, pencil hardness of 5H, and satisfactory drying and curing times of 2 h and 6 h, respectively. These properties satisfy the general performance requirements for protective epoxy coatings applied on steel substrates and are comparable to those reported in previous studies on epoxy-based anticorrosive coatings [22].

The excellent adhesion rating (5B) indicates strong interfacial bonding between the coating and steel substrate. This behavior is primarily attributed to the high polarity of the epoxy network and the effective crosslinking reaction between the YD-011X75 epoxy resin and the G-5022 curing agent. Strong adhesion is essential for corrosion-protection applications because it minimizes coating delamination and restricts the penetration of corrosive species to the metal surface. Similar adhesion performance has been reported for epoxy coatings reinforced with nanoclay and other inorganic fillers [22, 39].

The impact strength of 69 KG.cm demonstrates that the incorporation of TPP and clay effectively improved the toughness of the coating while maintaining structural integrity. Previous sections showed that TPP acts as a toughening modifier by reducing the brittleness of the epoxy network, whereas exfoliated clay nanosheets enhance stress transfer and hinder crack propagation. The relatively high impact strength observed in the coating formulation suggests that these reinforcement mechanisms remain effective even in the presence of pigments, fillers, solvents, and additives. Similar toughening effects have been reported for epoxy systems containing TPP [7] and nanoclay [38, 41].

The coating also exhibited a flexibility value of 2 mm and a pencil hardness of 5H, indicating a favorable balance between toughness and surface hardness. In epoxy coatings, improvements in toughness are often accompanied by reductions in hardness; however, the present formulation maintained high hardness while achieving good flexibility. This behavior suggests that the combined incorporation of TPP and clay contributes to stress redistribution without significantly compromising the rigidity of the crosslinked epoxy network.

Furthermore, the fineness of 25 μm confirms effective dispersion of pigments, fillers, and reinforcing additives during ball-milling. Uniform dispersion is critical for achieving consistent coating performance, as agglomerated particles can act as stress-concentration sites and reduce both mechanical and anticorrosive properties. The satisfactory drying and curing times further indicate that the addition of TPP and clay did not adversely affect the curing kinetics of the YD-011X75/G-5022 epoxy system.

Overall, the results demonstrate that the incorporation of 4 wt.% TPP and 1 wt.% clay enables the development of a multifunctional epoxy coating with excellent adhesion, good flexibility, high surface hardness, and enhanced impact resistance. These characteristics make the coating a promising candidate for long-term corrosion-protection applications on steel structures.

3.3. Thermal Properties of the Epoxy Composite Materials and Epoxy Paint Based on Kukdo YD-011X75/G-5022

Thermal Analysis of Kukdo YD-011X75/G-5022 Epoxy Composite Material

The thermal behavior of neat epoxy (EP, Kukdo YD-011X75/G-5022), epoxy containing 4 wt.% triphenyl phosphate (EP-TPP4, Kukdo YD-011X75/4%TPP/G-5022), and epoxy containing 1 wt.% clay (EP-Clay_1, Kukdo YD-011X75/1% Clay/G-5022) was investigated by simultaneous thermogravimetric analysis, differential scanning calorimetry, and derivative thermogravimetry (TG-DSC-dTG), as shown in Fig. 5.

The thermal behavior of the cured Kukdo YD-011X75/G-5022 (EP) epoxy system was evaluated using simultaneous thermogravimetric and differential scanning calorimetric analysis (TG-DSC), and the corresponding curves are presented in Fig. 5a. Three characteristic thermal events were observed on the DSC thermogram at 71.49°C, 395.65°C, and 442.15°C. The first thermal event appeared as a weak endothermic peak at 71.49°C and is attributed to the evaporation of residual solvent and low-molecular-weight volatile compounds trapped within the cured epoxy network. The absence of noticeable weight loss in the TG curve confirms that no significant degradation of the polymer structure occurred in this temperature region. This result indicates that the curing process between Kukdo YD-011X75 epoxy resin and G-5022 hardener was effective, producing a relatively stable crosslinked network with only a small amount of residual volatile species.

According to the TG curve, the cured epoxy system remained thermally stable up to approximately 292°C. No significant mass loss was detected below this temperature, indicating excellent thermal resistance under moderate thermal exposure. This behavior is characteristic of highly crosslinked epoxy

thermosets and can be attributed to the dense three-dimensional network generated during the epoxy-amine curing reaction. The aromatic rings present in the epoxy backbone further contribute to thermal stability by restricting chain mobility and increasing the energy required for bond cleavage. Similar thermal degradation behavior has been reported for aromatic epoxy systems cured with amine and polyamide hardeners [1, 2, 39].

The onset of thermal degradation occurred at approximately 292°C and was accompanied by an exothermic peak centered at 395.65°C. At this stage, the material experienced a weight loss of 16.29 wt.%, corresponding to a remaining mass of 83.71 wt.%. This degradation stage is mainly associated with the cleavage of relatively weak bonds within the crosslinked epoxy network, including ether linkages, hydroxyl-containing segments, and aliphatic structures generated during curing. Previous studies have shown that the initial degradation of epoxy thermosets generally begins with the scission of these thermally less stable groups before extensive decomposition of the aromatic network occurs [1, 2].

A second and more pronounced exothermic peak was observed at 442.15°C, corresponding to a cumulative weight loss of 58.13 wt.% (TG = 41.87%). This thermal event is attributed to the degradation of the primary epoxy backbone and aromatic crosslinked structure. The higher intensity of this peak indicates that the majority of thermal decomposition occurred within this temperature range. The decomposition of aromatic epoxy structures requires higher activation energy than that of aliphatic segments, explaining the elevated degradation temperature observed in this stage.

The temperatures corresponding to 10 wt.% and 50 wt.% mass loss were determined to be 377.01°C and 435.78°C, respectively. These values indicate that the cured Kukdo YD-011X75/G-5022 system possesses good thermal stability and maintains structural integrity over a broad temperature range. The relatively high T10% and T50% values reflect the effectiveness of the crosslinked epoxy network in resisting thermal degradation. Similar thermal resistance has been reported for epoxy systems containing aromatic epoxy resins and suitable curing agents that generate high crosslink densities [7, 22, 27].

A residual mass of 15.68 wt.% remained at 500°C after thermal decomposition. The formation of this residue is attributed to the carbonization of aromatic structures present in the cured epoxy network. During thermal degradation, portions of the aromatic backbone undergo cyclization and condensation reactions, producing thermally stable carbonaceous structures. The remaining char acts as a protective barrier that slows further degradation and contributes to the overall thermal stability of the material.

Comparison with previous studies indicates that the thermal stability of the present Kukdo YD-011X75/G-5022 system is comparable to that of other epoxy thermosets reported in the literature. Cuong et al. [7] reported enhanced thermal stability for DER 671X75/T31 systems, while Cuong et al. [22, 27] observed improved thermal resistance in epoxy composites containing nanosilica, zinc borate, and micaceous iron oxide. Although those systems incorporated additional fillers, the present unfilled epoxy

formulation still exhibited relatively high T10% and T50% values, demonstrating that the Kukdo YD-011X75/G-5022 network itself possesses excellent inherent thermal stability.

The influence of curing chemistry should also be considered. Miturska and Rudawska [39] demonstrated that the type of curing agent significantly affects the final structure and performance of epoxy materials. The thermal behavior observed in the present study suggests that G-5022 promotes the formation of a sufficiently dense and homogeneous crosslinked structure, thereby delaying thermal degradation and improving resistance to thermal decomposition.

Overall, the TG-DSC results demonstrate that the cured Kukdo YD-011X75/G-5022 epoxy system possesses good thermal stability, characterized by delayed degradation, high decomposition temperatures, and appreciable char formation. These properties are attributed primarily to the aromatic structure of the epoxy resin and the highly crosslinked network generated during curing with G-5022 hardener.

Effect of TPP on the Thermal Properties of Kukdo YD-011X75/TPP/G-5022 Epoxy Composite Materials

Among the investigated formulations, the epoxy composite containing 4 wt.% TPP (EP-TPP4) exhibited the best overall mechanical performance and was therefore selected for thermal characterization. The TG-DSC curves of the Kukdo YD-011X75/4 wt.% TPP/G-5022 epoxy composite are shown in Fig. 5b.

The TG-DSC results presented in Fig. 5b demonstrate that the incorporation of 4 wt.% TPP significantly enhances the thermal stability of the cured epoxy system. The Kukdo YD-011X75/4 wt.% TPP/G-5022 composite remained thermally stable up to approximately 300°C, with the onset of degradation occurring between 334°C and 338°C. The temperatures corresponding to 10 wt.% and 50 wt.% mass loss were determined to be approximately 379°C and 436°C, respectively. Furthermore, a residual mass of 29.37 wt.% was retained at 500°C, indicating the formation of a substantial amount of thermally stable char during decomposition.

Compared with the unmodified epoxy system (EP), the EP-TPP4 composite exhibited delayed thermal degradation and a significantly higher residual mass at elevated temperatures. The residual mass increased from 15.68 wt.% for the neat epoxy system to 29.37 wt.% for the TPP-containing composite, corresponding to an increase of approximately 87%. This remarkable increase suggests that TPP effectively modifies the degradation pathway of the epoxy matrix and promotes the formation of carbonaceous structures during thermal decomposition.

The improved thermal stability can be attributed to the phosphorus-containing structure of triphenyl phosphate. During thermal degradation, TPP undergoes decomposition to generate phosphorus-rich intermediates, including phosphoric and polyphosphoric acid species. These compounds catalyze dehydration, cyclization, and aromatization reactions within the epoxy matrix, thereby accelerating char formation and reducing the generation of volatile combustible products. As a result, a compact protective layer is formed on the material surface, limiting heat transfer and slowing the progression of

thermal degradation. This condensed-phase flame-retardant mechanism has been widely reported for phosphate-based flame retardants incorporated into epoxy thermosets.

The increase in thermal stability observed in the present study is consistent with previous findings reported by Cuong et al. [7], where the incorporation of TPP into DER 671X75/T31 epoxy systems significantly improved thermal degradation resistance and increased the thermal stability of the resulting composites. Although differences in resin chemistry and curing-agent structure lead to variations in decomposition temperatures, both studies confirm that TPP effectively promotes char formation and enhances the thermal resistance of epoxy networks.

The thermal stabilization mechanism of TPP differs from that reported for inorganic fillers such as nanosilica, zinc borate, and micaceous iron oxide [22, 27]. Inorganic fillers primarily improve thermal resistance through physical barrier effects that hinder heat transfer and restrict the diffusion of degradation products. In contrast, TPP acts through a phosphorus-mediated chemical mechanism that alters the degradation pathway of the polymer and promotes the formation of thermally stable char. Therefore, the enhanced thermal stability of the EP-TPP4 composite results from both the inherent crosslinked structure of the Kukdo YD-011X75/G-5022 epoxy network and the active char-forming capability of TPP.

The curing chemistry may also contribute to the observed behavior. Miturska and Rudawska [39] reported that the final thermal and mechanical performance of epoxy materials strongly depends on the curing agent and the resulting network architecture. The excellent thermal stability achieved in the present EP-TPP4 system suggests that the G-5022 curing agent generated a sufficiently dense crosslinked structure capable of efficiently interacting with TPP molecules and maximizing their thermal stabilization effect.

Overall, the results demonstrate that the incorporation of 4 wt.% TPP not only improves the mechanical performance of the epoxy coating but also substantially enhances its resistance to thermal degradation. The combination of delayed decomposition, higher thermal decomposition temperatures, and significantly increased char yield confirms the multifunctional role of TPP as both a toughening additive and an effective phosphorus-based thermal stabilizer for epoxy coating applications.

The thermal stability mechanism of phosphorus flame retardant compounds such as TPP in epoxy polymer substrates takes place according to the two mechanisms in Fig. 6.

The thermal stability mechanism of phosphorus-based flame retardants, such as triphenyl phosphate (TPP), primarily operates in the gas phase. Upon exposure to elevated temperatures, TPP undergoes thermal decomposition, generating reactive species such as $PO^{\bullet}$ and $PO_2^{\bullet}$ radicals. These radicals interact with combustion generated species like $H^{\bullet}$ and $OH^{\bullet}$, effectively neutralizing them and reducing the number of active centers that drive polymer degradation. This process inhibits the release of volatile degradation products and limits oxygen diffusion into the combustion zone, thereby suppressing flame propagation [23–24].

In addition to its gas phase activity, TPP also contributes to flame retardancy in the condensed phase. At high ignition temperatures, phosphorus-containing compounds decompose to form phosphoric acid, which promotes char formation. This char acts as a protective barrier, forming a glassy layer that slows down pyrolysis, the breakdown of polymer chains and release of flammable gases. Furthermore, the release of water radicals during decomposition helps dilute oxygen, reducing its availability for combustion. The resulting char layer plays a crucial role in fire resistance, prevents the movement of flammable gases and heat, blocks the formation of new radicals, and protects the underlying polymer from thermal degradation [23–26].

A notable effect of TPP incorporation is the significant increase in char yield after thermal degradation. Although the T10% and T50% values of the EP-TPP4 composite increased only slightly compared with those of the neat epoxy system, the residual mass at 500°C increased from 15.68 wt.% to 29.37 wt.%, corresponding to an enhancement of approximately 87.3%. This result indicates that the primary contribution of TPP is not merely delaying thermal decomposition but promoting the formation of thermally stable carbonaceous structures during degradation.

Similar trends have been reported for phosphorus-containing epoxy systems and phosphate-based flame retardants [23–26, 28–30, 32, 35], where the incorporation of organophosphorus compounds significantly increased char formation while producing only moderate changes in decomposition temperatures. During thermal degradation, TPP generates phosphorus-containing intermediates that catalyze dehydration, cyclization, and aromatization reactions, thereby favoring carbonization of the epoxy matrix and suppressing the evolution of combustible volatile products. Consequently, a protective char layer is formed, which retards heat transfer and slows further degradation.

The present findings are consistent with our previous studies on TPP-modified epoxy systems [7], which also demonstrated improved thermal stability and enhanced residue formation after decomposition. Compared with epoxy composites containing nanosilica, zinc borate, montmorillonite, and micaceous iron oxide [22, 27], the stabilization mechanism of TPP is fundamentally different. Whereas inorganic fillers mainly improve thermal resistance through physical barrier effects, TPP acts predominantly through a phosphorus-mediated chemical pathway that promotes condensed-phase carbonization. Furthermore, the favorable thermal behavior observed in the present work may also be associated with the crosslinked network generated by the G-5022 curing agent, whose influence on the thermal durability of epoxy systems has been highlighted in previous studies [39]. Therefore, the enhanced thermal stability of the EP-TPP4 composite can be attributed to the synergistic effect between phosphorus-assisted char formation and the highly crosslinked aromatic epoxy network.

Effect of Clay on the Thermal Properties of Kukdo YD-011X75/G-5022 Epoxy Composite Materials

Based on the mechanical property results presented in Table 1, the epoxy composite containing 1 wt.% clay (EP-Clay_1) exhibited the most favorable overall performance, particularly in terms of impact resistance while maintaining excellent flexibility, adhesion, and hardness. Therefore, this formulation was selected as the optimum composition for further thermal characterization. The thermal stability and

degradation behavior of the Kukdo YD-011X75/1 wt.% clay/G-5022 epoxy nanocomposite were subsequently investigated using simultaneous thermogravimetric and differential scanning calorimetric analysis (TG-DSC), and the corresponding curves are shown in Fig. 5c.

The TG-DSC results presented in Fig. 5c indicate that the EP-Clay_1 nanocomposite exhibits good thermal stability over a broad temperature range. The material remained thermally stable up to approximately 300°C, while the onset of significant thermal degradation occurred at 341.74–343°C. The temperature corresponding to 50 wt.% mass loss (T50%) was determined to be 438.49°C, and a residual mass of 23.77 wt.% remained at 500°C. These values demonstrate that the incorporation of 1 wt.% clay effectively improved the thermal resistance of the Kukdo YD-011X75/G-5022 epoxy system.

The enhanced thermal stability can be attributed primarily to the exfoliated nanostructure confirmed by XRD and TEM analyses. The homogeneous dispersion of high-aspect-ratio clay nanosheets throughout the epoxy matrix creates a tortuous pathway that restricts the diffusion of heat, oxygen, and volatile degradation products. Consequently, thermal decomposition is delayed and the degradation rate is reduced. In addition, the dispersed clay layers promote the formation of a protective carbonaceous–silicate barrier during thermal decomposition, which further inhibits heat transfer and mass transport between the degrading polymer and the surrounding environment [3–6, 14–16, 20–21].

The present results are consistent with previous studies on epoxy/clay nanocomposites. Su et al. [38] reported that functionalized montmorillonite improved the thermal stability and glass-transition temperature of epoxy nanocomposites as a result of enhanced filler dispersion and stronger filler–matrix interactions. Similarly, Altaf et al. [40] observed increased char yield and improved flame-retardant performance in organoclay/epoxy nanocomposites, attributing these effects to the barrier action of well-dispersed clay layers. The relatively high residual mass observed in the present study supports a similar stabilization mechanism.

Furthermore, Örçen and Bayram [41] demonstrated that epoxy composites containing 1 wt.% nanoclay exhibited the most favorable balance of mechanical and thermal properties, whereas higher clay loadings resulted in reduced efficiency due to particle agglomeration and deterioration of filler dispersion. This observation agrees well with the present results, where the 1 wt.% clay formulation provided both the highest impact strength and improved thermal stability. Likewise, Miturska and Rudawska [39] reported that the effectiveness of montmorillonite reinforcement strongly depends on both filler dispersion and the characteristics of the cured epoxy network. The enhanced thermal resistance observed in the EP-Clay_1 nanocomposite therefore appears to arise from the synergistic effect of the exfoliated clay morphology and the highly crosslinked Kukdo YD-011X75/G-5022 epoxy network.

Overall, the thermal analysis confirms that the incorporation of a small amount of well-dispersed clay (1 wt.%) is sufficient to significantly improve the thermal stability of the epoxy system. The observed enhancement is primarily associated with the formation of an exfoliated nanostructure, which acts as an efficient barrier against heat and mass transport during thermal degradation.

Comparison of thermal stability between epoxy composite materials

The thermal stability of the epoxy composite materials YD-011X75/G-5022 (EP sample), YD-011X75/4% TPP/G-5022 (EP-TPP4 sample), and YD-011X75/1% clay/G-5022 (EP-Clay_1 sample) is illustrated in Fig. 5d.

The thermogravimetric (TG) curves presented in Fig. 5d indicate that all investigated epoxy systems exhibit good thermal stability, with the onset of significant thermal degradation occurring at approximately 300°C. However, noticeable differences in degradation behavior are observed among the samples. Compared with the neat epoxy system (EP), the composites containing 1 wt.% clay (EP-Clay_1) and 4 wt.% triphenyl phosphate (EP-TPP4) exhibit improved thermal resistance, as evidenced by their higher degradation temperatures and increased residual mass at elevated temperatures.

The enhanced thermal stability of EP-Clay_1 can be attributed to the exfoliated clay nanostructure confirmed by XRD and TEM analyses. The uniformly dispersed clay nanosheets create a tortuous pathway that restricts heat transfer and hinders the diffusion of oxygen and volatile degradation products through the epoxy matrix. Consequently, the thermal decomposition process is delayed, and the degradation rate is reduced. Similar thermal stabilization mechanisms have been reported for montmorillonite-reinforced epoxy nanocomposites by Su et al. [38], Altaf et al. [40], and Örçen and Bayram [41].

In contrast, the improved thermal performance of EP-TPP4 originates primarily from the phosphorus-containing structure of triphenyl phosphate. During thermal degradation, TPP promotes dehydration, cyclization, and aromatization reactions, facilitating the formation of a thermally stable carbonaceous char layer. This protective char barrier suppresses the release of combustible volatile compounds and limits heat transfer to the underlying material. Similar phosphorus-induced char-forming mechanisms have been widely reported for phosphate-based flame-retardant epoxy systems [7, 23–26, 33–35, 40].

Although both additives enhance the thermal stability of the epoxy matrix, their stabilization mechanisms are fundamentally different. Clay acts predominantly through a physical barrier effect, whereas TPP modifies the degradation pathway through chemical promotion of char formation. Therefore, the improved thermal resistance observed for EP-Clay_1 and EP-TPP4 demonstrates the effectiveness of both nanoclay and phosphorus-containing additives in enhancing the thermal durability of epoxy coatings through complementary stabilization mechanisms.

Thermal Properties of Kukdo YD-011X75/4% TPP/1% Clay/G-5022 Epoxy Composite Material and Epoxy Paint

Thermal Properties of Kukdo YD-011X75/4% TPP/1% Clay/G-5022 Epoxy Composite Material

To evaluate the combined effects of TPP and nanoclay on the thermal stability of the epoxy system, the optimized formulation containing 4 wt.% TPP and 1 wt.% clay (EP-TPP4-Clay_1), together with the epoxy

paint formulation (EP paint), was subjected to TG-dTG and TG-DSC analyses. The thermal degradation behavior and calorimetric characteristics of these systems are presented in Fig. 7.

The thermal analysis results presented in Fig. 7a indicate that the epoxy composite material composed of Kukdo YD-011X75, 4 wt.% TPP, and 1 wt.% clay (EP-TPP4-Clay_1) exhibits satisfactory thermal stability. Initial thermal decomposition begins with solvent evaporation occurring between 61.09°C and 127.95°C. The material remains stable up to approximately 327.36°C. A 10 wt.% mass loss is observed at 359.2°C, while 50 wt.% mass loss occurs at 434.15°C. At 500°C, the residual mass is approximately 13.22 wt.%. An exothermic peak is detected at 644.82°C on the DSC curve; however, the absence of a corresponding signal on the dTG curve suggests that this peak may result from instrumental background interference rather than a material-specific thermal event.

The thermal degradation profile of EP-TPP4-Clay_1 is generally comparable to those observed for the EP-TPP4 and EP- Clay-1 systems. The T10% and T50% values remain within a similar range, indicating that the simultaneous incorporation of TPP and clay does not substantially alter the onset or main degradation stages of the epoxy network. This behavior suggests that the thermal stability of the Kukdo YD-011X75/G-5022 epoxy system is primarily governed by the highly crosslinked aromatic structure of the cured resin, while the addition of TPP and clay mainly influences the degradation mechanism rather than dramatically shifting the degradation temperatures.

The absence of a significant increase in T10% and T50% is consistent with previous studies on phosphorus-containing epoxy systems and epoxy/clay nanocomposites. Cuong et al. [7] reported that TPP improved the thermal degradation resistance of epoxy materials mainly through modification of the decomposition pathway and promotion of char formation rather than through a substantial increase in degradation temperature. Similarly, Su et al. [38], Altaf et al. [40], and Örçen and Bayram [41] observed that nanoclay primarily acts as a barrier phase that restricts heat and mass transport during decomposition, while only moderately affecting the onset degradation temperature.

The present results further indicate that the principal advantage of combining TPP and clay lies in the remarkable enhancement of mechanical performance rather than in a substantial increase in thermal resistance. Compared with the neat epoxy coating, the EP-TPP4-Clay_1 formulation exhibited an impact strength of 100 KG.cm, corresponding to an improvement of approximately 194%, whereas the thermal stability remained comparable to that of the EP-TPP4 and EP-Clay_1 systems. This observation suggests that the reinforcing mechanisms of TPP and clay are particularly effective in improving toughness and impact resistance through stress-transfer enhancement, crack deflection, and energy-dissipation processes.

Furthermore, previous studies have demonstrated that clay platelets improve mechanical performance by reinforcing the epoxy network and inhibiting crack propagation [38, 39, 41], while phosphorus-containing additives such as TPP contribute to toughness enhancement by reducing the brittleness of highly crosslinked epoxy structures [7, 23–26, 33–35]. The simultaneous incorporation of these two additives therefore generates a synergistic mechanical reinforcement effect, even though their combined

influence on thermal stability is relatively limited. Consequently, the EP-TPP4-Clay_1 formulation offers an attractive balance between mechanical durability and thermal resistance, making it a promising candidate for high-performance protective coating applications.

Thermal Properties of Kukdo YD-011X75/G-5022 epoxy paint (EP Paint)

The thermal behavior of the Kukdo YD-011X75/4% TPP/1% clay/G-5022 epoxy paint is illustrated in Fig. 7b.

The thermal analysis results presented in Fig. 7b demonstrate that the formulated epoxy coating possesses excellent thermal stability and resistance to thermal degradation. The broad endothermic region observed between approximately 95°C and 239°C is primarily associated with the evaporation of residual solvents and low-molecular-weight volatile species remaining within the coating matrix. No significant mass loss was detected within this temperature range, indicating that the cured epoxy network remained structurally stable during heating.

The onset of substantial thermal degradation occurred at relatively high temperatures, with T10% and T50% values of 323.8°C and 465.42°C, respectively. These values are characteristic of highly crosslinked aromatic epoxy systems and confirm that the incorporation of TPP and clay did not adversely affect the thermal integrity of the coating. More importantly, the T50% value of 465.42°C is considerably higher than those obtained for the corresponding epoxy films, indicating that the coating formulation exhibits improved resistance to thermal decomposition at elevated temperatures.

A particularly noteworthy result is the residual mass of 47.54 wt.% at 500°C, which is substantially higher than that observed for the epoxy composite films. This behavior can be attributed not only to the phosphorus-assisted char-forming action of TPP but also to the presence of thermally stable inorganic components, including clay, iron oxide, zinc phosphate, and talc. During thermal decomposition, the organic epoxy matrix undergoes degradation, whereas these inorganic constituents remain stable and contribute to the formation of a protective residue layer. Consequently, the coating exhibits enhanced resistance to mass loss and thermal degradation.

The thermal stabilization mechanism of the coating is therefore more complex than that of the epoxy composite films. TPP promotes carbonization and the formation of a protective char layer through phosphorus-containing intermediates, while exfoliated clay nanosheets act as physical barriers that hinder heat transfer and suppress the diffusion of volatile degradation products. Similar barrier effects of nanoclay have been reported in epoxy nanocomposites by Su et al. [38], Altaf et al. [40], and Örçen and Bayram [41]. In addition, inorganic pigments and fillers further contribute to thermal resistance by increasing the amount of non-combustible residue remaining after decomposition.

These observations are consistent with previous studies on epoxy coatings containing TPP, nanosilica, zinc borate, and inorganic pigments [7, 22, 27]. Cuong et al. [7] reported that phosphorus-containing additives promoted char formation and improved thermal degradation resistance, while Cuong et al. [22,

27] demonstrated that inorganic fillers and pigments enhanced thermal stability through barrier and residue-forming mechanisms. The present results indicate that combining TPP, nanoclay, anticorrosive pigments, and mineral fillers provides multiple thermal stabilization pathways operating simultaneously.

Overall, the high T50% value and exceptionally high residual mass at 500°C confirm that the developed coating possesses superior thermal resistance compared with the corresponding epoxy composite films. The synergistic contribution of the phosphorus-based additive (TPP), exfoliated clay nanosheets, and thermally stable inorganic pigments/fillers results in a coating system capable of maintaining structural integrity under severe thermal conditions. Such characteristics are highly desirable for protective coatings intended for long-term service in demanding industrial environments.

Analysis of the data presented in Table 3 demonstrates that the incorporation of triphenyl phosphate (TPP) and nanoclay significantly influences the thermal degradation behavior of the Kukdo YD-011X75/G-5022 epoxy system. Compared with the neat epoxy resin (EP), both EP-TPP4 and EP-Clay_1 exhibited delayed thermal degradation, as evidenced by the increase in the onset decomposition temperature from 292°C to approximately 334–338°C and 342–343°C, respectively. In addition, the temperatures corresponding to 10 wt.% and 50 wt.% mass loss increased slightly, indicating improved resistance to thermal decomposition.

Table 3
Thermal properties of Kukdo YD-011X75/TPP/clay/G-5022 epoxy composite materials and epoxy paint

Sample	**Temperature begins to decompose (^oC)**	**Decomposition Temperature of 10 wt.% (^oC) (T10%)**	**Decomposition Temperature of 50 wt.% (^oC) (T50%)**	**Residual mass at 500^oC (wt.%)**
EP	292^oC	377.01	435.78	15.68
EP-TPP4	334–338	379.378	436.6327	29.37
EP-Clay_1	341.74–343	380.6054	438.4868	23.77
EP-TPP4-Clay_1	61.09-127.95	359.2	434.15	13.22
EP paint	95–239	323.8	465.418	47.54

The most pronounced effect of TPP was observed in the residual mass at 500°C. The char yield increased from 15.68 wt.% for the neat epoxy system to 29.37 wt.% for EP-TPP4, corresponding to an increase of approximately 87%. This result confirms that TPP promotes condensed-phase stabilization through phosphorus-assisted carbonization reactions. During thermal decomposition, phosphorus-containing intermediates generated from TPP facilitate dehydration, cyclization, and aromatization of the epoxy network, leading to the formation of thermally stable carbonaceous structures [23–26]. Similar thermal stabilization mechanisms were reported in our previous study on DER 671X75/T31/TPP

systems [7], where TPP significantly improved thermal degradation resistance and enhanced char formation.

The incorporation of 1 wt.% clay also improved thermal stability, increasing the onset decomposition temperature to approximately 342°C and the residual mass at 500°C to 23.77 wt.%. This behavior is consistent with previous reports on epoxy/clay nanocomposites [38–41], in which exfoliated silicate layers acted as effective barrier structures that restricted heat transfer and reduced the diffusion rate of volatile degradation products. Su et al. [38] reported that functionalized montmorillonite enhanced the thermal stability and glass-transition temperature of epoxy systems, while Örçen and Bayram [41] observed improved thermal resistance at nanoclay contents close to 1 wt.%, corresponding closely to the optimum clay loading identified in the present work.

Interestingly, the hybrid EP-TPP4-Clay_1 system did not exhibit a further increase in thermal stability compared with EP-TPP4 and EP-Clay_1. The T10% and T50% values decreased slightly to 359.2°C and 434.15°C, respectively, while the residual mass at 500°C was reduced to 13.22 wt.%. This observation suggests that although TPP and clay exhibit a strong synergistic effect on mechanical reinforcement, the same synergism is not fully realized in terms of thermal stability. The interaction between phosphorus-containing degradation products and clay surfaces may alter the decomposition pathway, resulting in a more complex thermal behavior than that observed in the individual filler systems.

In contrast, the epoxy paint formulation (EP paint) exhibited the highest thermal resistance among all investigated samples. The temperature corresponding to 50 wt.% mass loss reached 465.42°C, while the residual mass at 500°C increased dramatically to 47.54 wt.%. This outstanding thermal performance cannot be attributed solely to TPP and clay. Rather, it results from the combined contribution of the epoxy matrix, phosphorus-containing TPP, exfoliated clay layers, and thermally stable inorganic constituents such as iron oxide, zinc phosphate, and talc. These inorganic components remain largely intact during thermal decomposition and contribute significantly to the formation of a protective residue layer.

Similar trends have been reported for epoxy coatings containing inorganic fillers, nanosilica, zinc borate, and layered silicates [22, 27, 38–41]. In such systems, thermal stabilization arises from multiple mechanisms operating simultaneously, including phosphorus-induced char formation, barrier effects associated with nanoclay, and the accumulation of thermally stable inorganic residues. The exceptionally high residual mass of 47.54 wt.% observed for EP paint therefore reflects the combined action of these mechanisms and demonstrates the effectiveness of the developed formulation for high-temperature protective coating applications.

Overall, the results indicate that TPP is the most effective additive for promoting char formation, whereas nanoclay primarily delays thermal degradation through barrier effects. The incorporation of both additives, together with inorganic pigments and fillers in the coating formulation, generates a multifunctional protective system with enhanced thermal durability and excellent resistance to thermal

decomposition. This behavior is consistent with previous studies involving phosphorus-containing flame retardants [7, 23–26], inorganic fillers [22, 27], and epoxy/clay nanocomposites [38–41].

3. Conclusion

The effects of triphenyl phosphate (TPP) and montmorillonite (MMT) clay on the mechanical and thermal properties of Kukdo YD-011X75/G-5022 epoxy materials and coatings were investigated. XRD and TEM analyses confirmed the successful exfoliation and uniform dispersion of clay within the epoxy matrix. The incorporation of 4 wt.% TPP and 1 wt.% clay individually increased the impact strength from 34KG.cm to 55 KG.cm and 50 KG.cm, respectively. A pronounced synergistic effect was observed when both additives were combined, resulting in an impact strength of 100 KG.cm, corresponding to a 194.1% improvement over the neat epoxy system. Thermal analysis demonstrated that TPP and clay enhanced the thermal stability of the epoxy materials. The epoxy coating containing 4 wt.% TPP and 1 wt.% clay exhibited excellent thermal resistance, with a T50% value of 465.42°C and a residual mass of 47.54 wt.% at 500°C. These results demonstrate that the combined use of TPP and montmorillonite clay is an effective approach for developing epoxy coatings with improved toughness and thermal durability, making them promising candidates for heat-resistant protective coating applications.

4. MATERIALS AND METHODS

4.1. Materials

The epoxy resin employed in this study was Kukdo YD-011X75 (Korea), characterized by an epoxy equivalent weight (EEW) ranging from 450 to 500 g/eq, a viscosity of 8,000–13,000 cPs at 25°C, a density between 1.16 and 1.20 g/cm³ at 20°C, and a non-volatile content of 75 ± 1 wt.%. The curing agent used was Kukdo G-5022 (Korea), a polyamide-based compound with an amine hydrogen equivalent weight (AHEW) of 165–185 g/eq, an amine number of 200–240 mg KOH/g, and a viscosity of 50,000–70,000 mPa.s at 40°C. This agent, composed of macro viscosity amines, provides enhanced flexibility, extended shelf life, and superior compatibility with solid epoxy resins.

Montmorillonite clay (Bentonite), sourced from India and having a purity exceeding 99%, was incorporated as a reinforced filler. Triphenyl phosphate (TPP), with a purity above 99% and obtained from China, served as the flame-retardant additive. Added components included iron oxide pigment (purity above of 99%, China), zinc phosphate (purity above of 99%, China), Bengel 908 bentonite (China) as a rheological modifier, SilTech C1700 (Canada) as a defoaming agent, Talc 1201 (China) as a filler, and xylene (China) as the solvent.

4.2. Preparation of Experimental Samples

4.2.1. Dispersion of Triphenyl Phosphate (TPP) into Epoxy Resin

To investigate the dispersion behavior of triphenyl phosphate (TPP) within the epoxy resin, 4.00 g of TPP was incorporated into 100.00 g of Kukdo YD-011X75 epoxy resin in a 250 mL glass beaker. The TPP concentration was maintained at 4.0 wt.%. The mixture was initially stirred using a mechanical stirrer at 500 rpm for 15 minutes, followed by an increase in stirring speed to 1000 rpm for a period of 90 minutes. Subsequently, the dispersion was subjected to ultrasonic treatment for 40 minutes to enhance homogeneity. Epoxy resin samples containing 2 wt.%, 4 wt.%, and 6 wt.% TPP were prepared for subsequent characterization.

4.2.2. Dispersion of Montmorillonite Clay into Epoxy Resin

For the clay dispersion study, 1.00 g of Montmorillonite clay was added to 100.00 g of Kukdo YD-011X75 epoxy resin in a 250 mL glass beaker, corresponding to a concentration of 1.0 wt.%. The mixture was stirred mechanically at 250 rpm for 15 minutes, followed by an increase to 1500 rpm for 150 minutes. Ultrasonic vibration was then applied for 60 minutes to promote uniform distribution of the clay particles. Added epoxy resin samples containing 1.0 wt.%, 2.5 wt.%, and 3 wt.% clay was also prepared for comparative analysis.

4.2.3. Co-Dispersion of TPP and Clay into Epoxy Resin

The co-dispersion process involved sequential incorporation of the additives. Initially, 1.00 g of Montmorillonite clay was dispersed into 100.00 g of epoxy resin following the procedure outlined in section 2.2.2. Subsequently, 4.00 g of TPP was introduced into the 1.0 wt.% clay/epoxy mixture using the method described in section 2.2.1. This process yielded a composite formulation designated as epoxy/4%TPP/1% clay.

4.2.4. Preparation of Polymer Composite Samples for Analysis

The epoxy resin (Kukdo YD-011X75) was cured using the polyamide curing agent (Kukdo G-5022) at ambient temperature for 6 hours. Post curing was conducted at 65°C for 60 minutes to ensure complete crosslinking. Thin film specimens with an approximate thickness of 50 µm were fabricated for Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) imaging. Fully cured samples were used for Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Derivative Thermogravimetry (DTG), and X-ray Diffraction (XRD) measurements.

Steel substrates were prepared according to standard, including mechanical abrasion via sanding, solvent cleaning with acetone, and thermal drying at 80°C. The polymer coatings were applied to the treated steel surfaces, ensuring a final dry film thickness in the range of 80–130 µm.

4.3. Analytical Methods and Characterization of Polymer Composite Materials

The dispersion processes were conducted using a mechanical stirrer (IKA RW 20, Germany) and an ultrasonic homogenizer (Sonics Vibram, Model CV334, USA), operating at a frequency of 50 kHz. The

quality of TPP dispersion within the epoxy matrix was examined via Scanning Electron Microscopy (SEM) using a Jeol JSM-IT200 instrument (Japan). The dispersion state of the clay within the epoxy matrix was characterized by X-ray diffraction (XRD) using a D2 Phaser diffractometer (Bruker, Germany) and Transmission Electron Microscopy (TEM, JEM-1400, JEOL, Japan). The thermal characterization of the polymer composites was performed using Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and Derivative Thermogravimetry (DTG). These analyses were carried out using a Setaram Labsys Evo TG-DSC analyzer, capable of operating up to a maximum temperature of 1600°C.

4.4. Standards for Mechanical Property Evaluation of Polymer Films and Coatings

The mechanical properties of the polymer coatings were assessed following international and national standards. Flexibility (bending resistance) was measured following ISO 1519:2002 using the Erichsen Model 266. Impact strength was evaluated according to ISO 6272:2002 with the Erichsen Model 304. Adhesion was figured out based on ASTM D3359-93 using the Erichsen Model 295. Pencil hardness was assessed following the JIS K5400-90 standard. Dry film thickness was measured using a MiniTest 3100 thickness gauge, following the Vietnamese National Standard TCVN 9406:2012.

Declarations

Availability of data

The data used to support this study are included within the article and are available from the corresponding author upon request.

Competing interests

The authors declare no competing financial interest.

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Authors Contributions

Conceptualization: [Cuong Huynh Le Huy], [Vinh Mai Phuc], [An Truong Thanh]; Methodology: [Cuong Huynh Le Huy]; Formal analysis and investigation: [Cuong Huynh Le Huy]; Data curation:[Cuong Huynh Le Huy], [Vinh Mai Phuc], [An Truong Thanh]; Data curation: [Cuong Huynh Le Huy], [Vinh Mai Phuc], [An Truong Thanh]; Funding acquisition: [NA, not applicable]; Resources: [Cuong Huynh Le Huy], [Vinh Mai Phuc], [An Truong Thanh]; Project administration: [Cuong Huynh Le Huy]; Software: [Cuong Huynh Le

Huy]; Supervision: [Cuong Huynh Le Huy]; Validation:[Cuong Huynh Le Huy]; Visualization: [Cuong Huynh Le Huy]; Writing – original draft preparation:[Cuong Huynh Le Huy], [Vinh Mai Phuc]; Writing – review & editing: [Cuong Huynh Le Huy].

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Figures

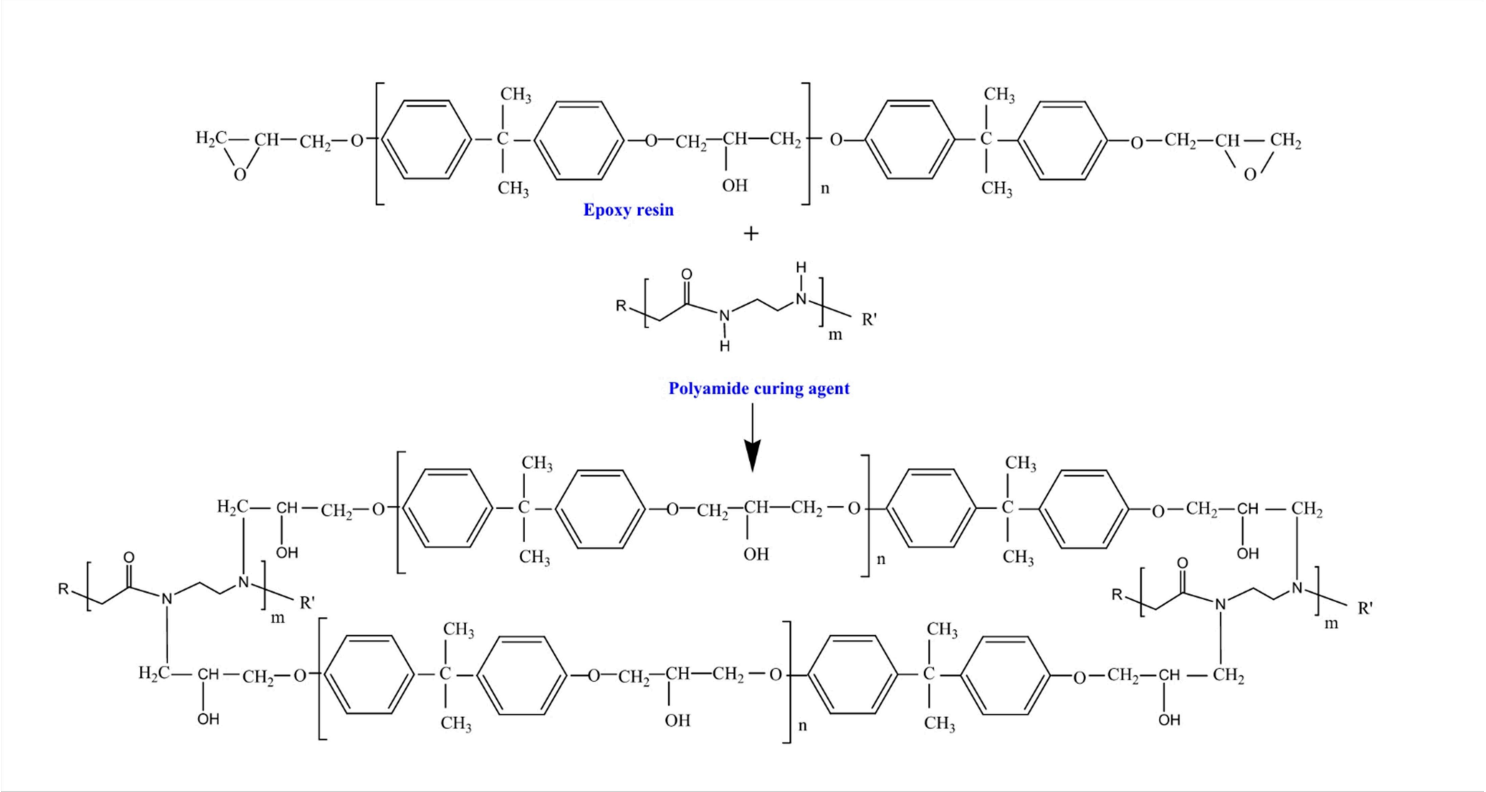


Figure 1

The curing reaction of Kukdo YD-011X75 epoxy resin with Kukdo G-5022 polyamide hardener

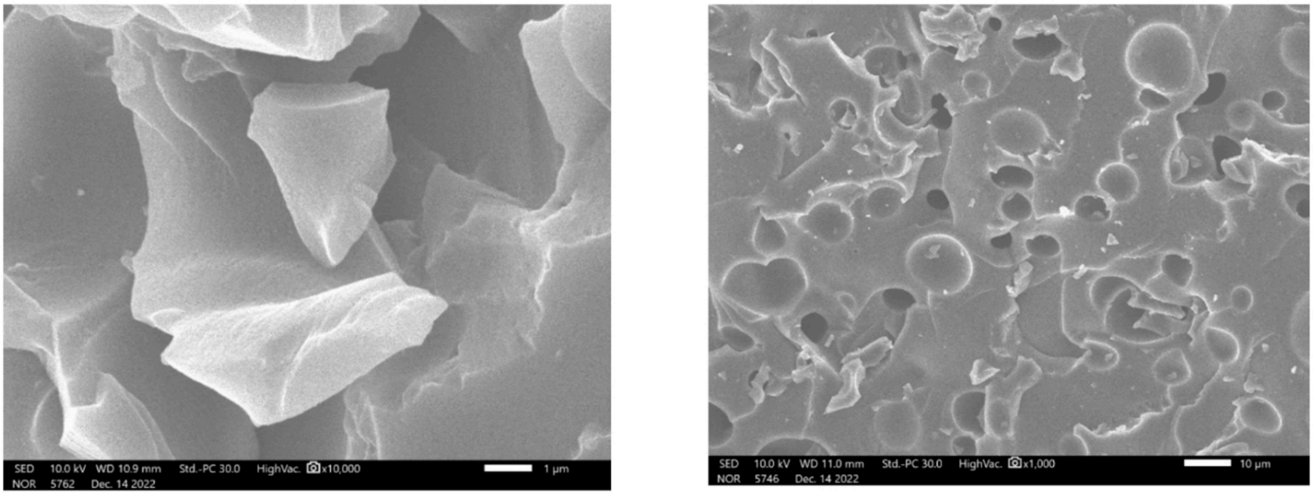


Figure 2

SEM image of Kukdo YD-011X75/4 wt.% TPP/G-5022 epoxy composite material

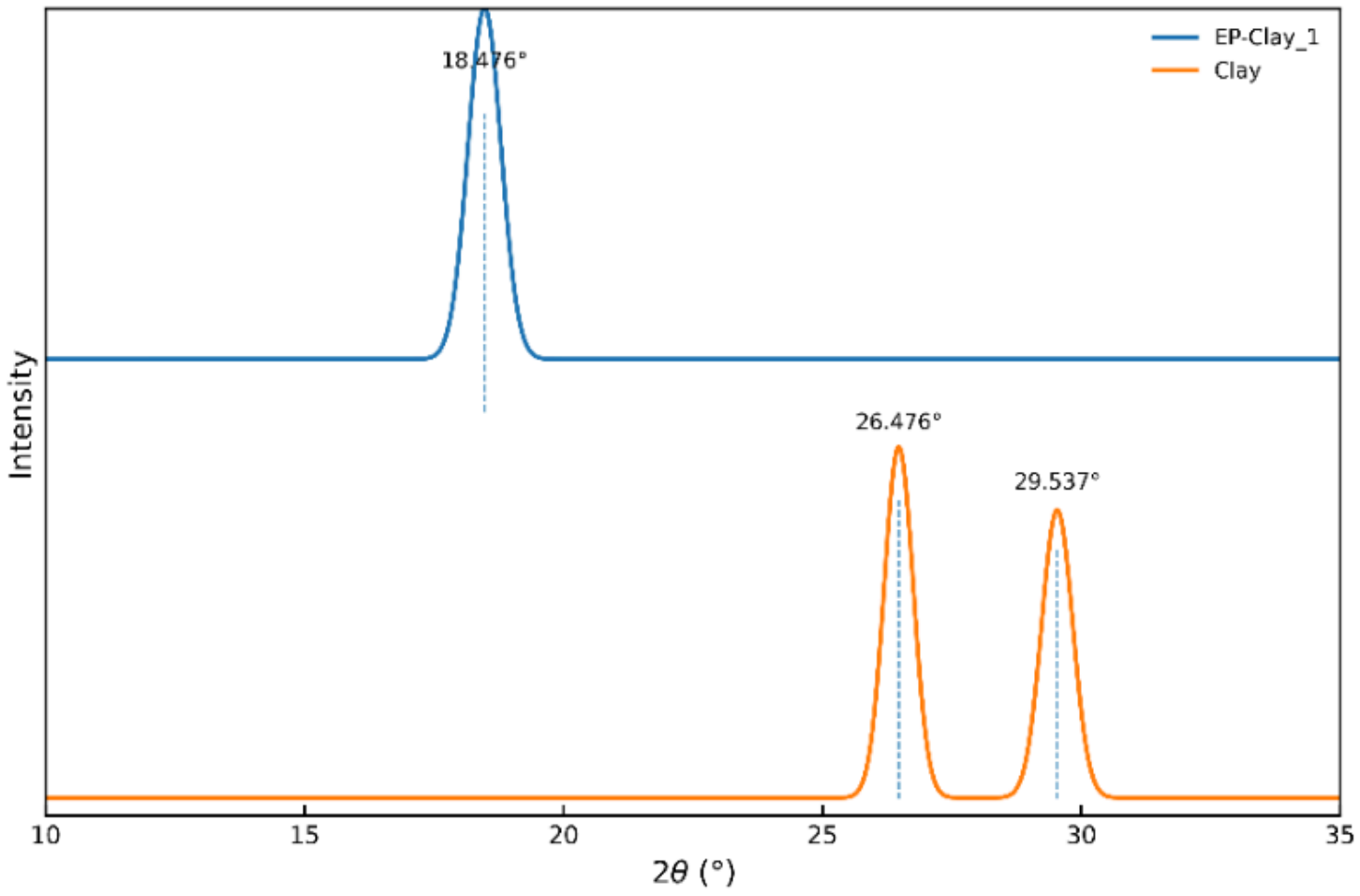


Figure 3

XRD curve of clay and EP_clay 1 samples

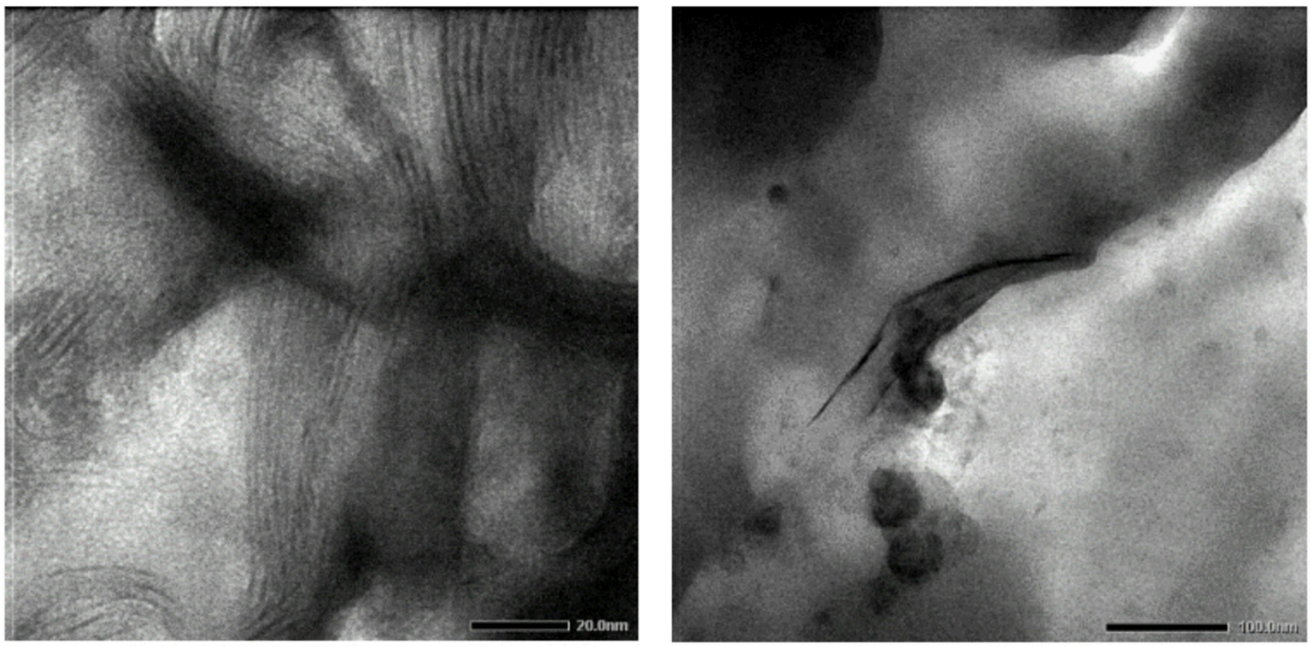


Figure 4

TEM image of epoxy composite Kukdo YD 011X75/1% clay/G-5022

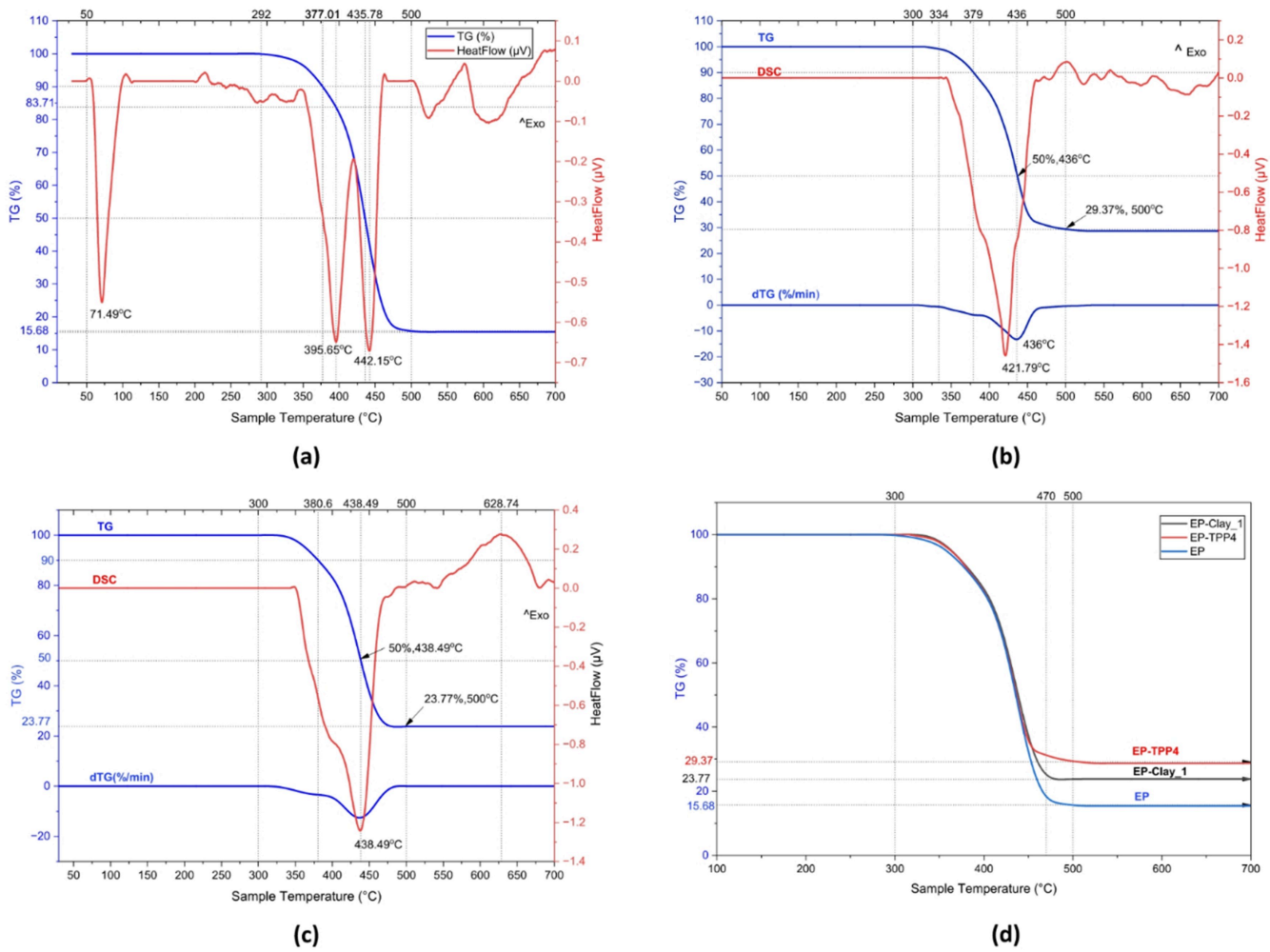


Figure 5

Thermal analysis of (a) EP (Kukdo YD-011X75/G-5022), (b) EP-TPP4 (Kukdo YD-011X75/4 % TPP/G-5022), (c) EP-Clay_1 (Kukdo YD-011X75/1 % Clay/G-5022), and (d) comparison of the thermal behavior of the epoxy systems.

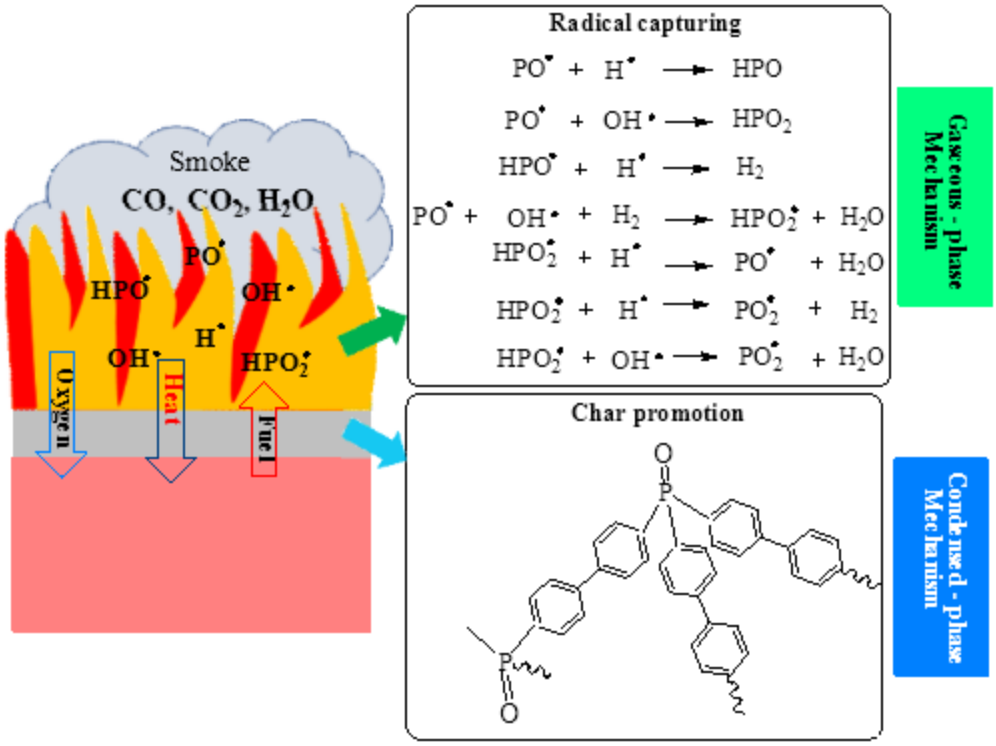


Figure 6

Thermal stability mechanism epoxy composite material reinforced with phosphorus flame retardant compounds

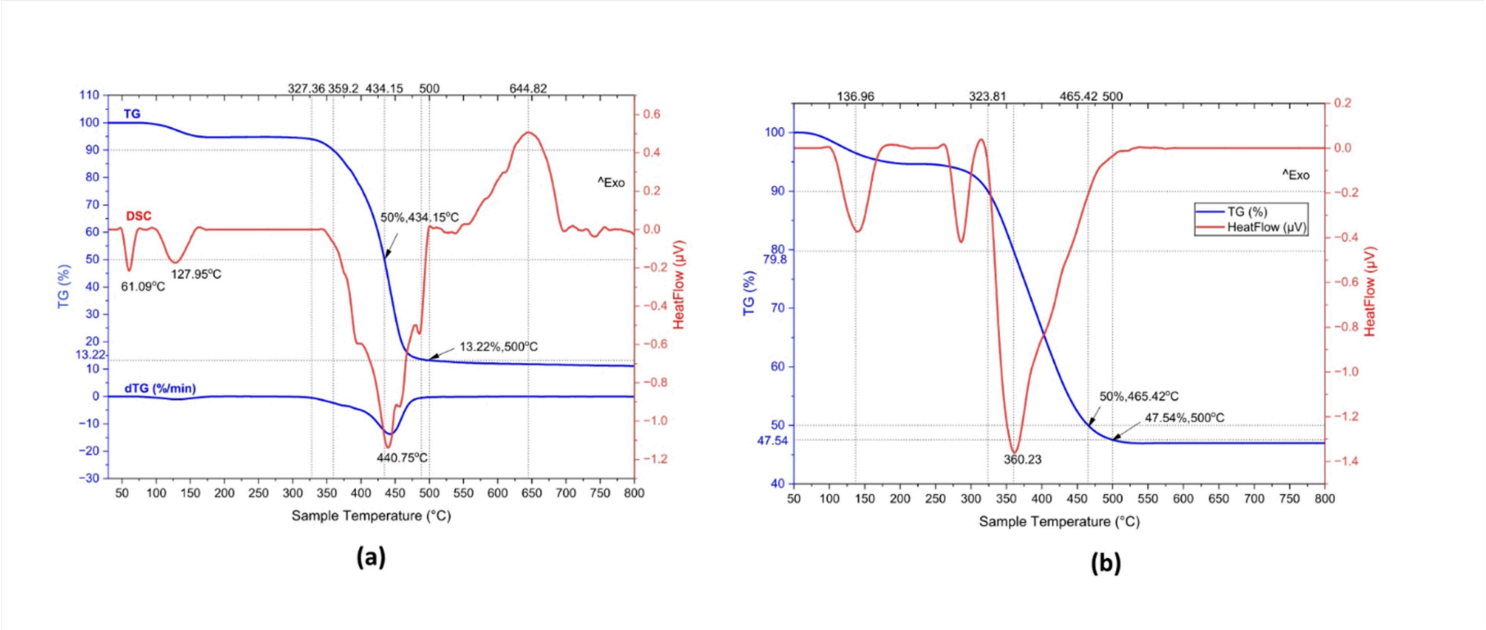


Figure 7

Thermal analysis of (a) EP-TPP4-Clay_1 (Kukdo YD-011X75/4 % TPP/1 % Clay/G-5022) and (b) EP paint.

Supplementary Files

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- floatimage1.png