Ramin Riahipour, Abolfazl Alizadeh Sahraei, Nekoda van de Werken, Mehran Tehrani, Karen Abrinia and Majid Baniassadi*

Improving flame-retardant, thermal, and mechanical properties of an epoxy using halogen-free fillers

https://doi.org/10.1515/secm-2017-0131
Received April 11, 2017; accepted August 12, 2017; previously published online October 17, 2017

Abstract: Various nano- and micro-sized fillers can be integrated into polymers to enhance their flame-retardant performance. In this work, a diglycidyl-ether bisphenol A epoxy was used as the matrix and nanostructured silica aerogel (AG) and ammonium polyphosphate (APP) microparticles were investigated as fillers to improve the flame-retardant and thermal properties of the epoxy. The anti-flame, thermal, and mechanical properties of the composites were investigated for different volume fractions of filler particles. It was found that APP decreased the burning rate while significantly improving the thermal stability. To investigate the flame resistant properties of combined AG and APP, an optimized ratio of AG and APP was added to the epoxy, leading to a stable flame-retardant epoxy with a low thermal conductivity and improved glass transition temperature (T_g). The synergy between the AG and APP in composite samples resulted in an interesting burning behavior where sample core was relatively less deteriorated compared with the samples containing only APP or AG. This was attributed to the decrease of thermal conductivity due to the addition of AG. Lastly, samples containing APP showed the highest limiting oxygen index percentage and it was found that only small amounts of APP are required to make the epoxy flame-retardant.

Keywords: ammonium polyphosphate (APP); epoxy; flame-retardant; silica aerogel; thermal properties.

1 Introduction

While polymeric materials possess unique advantages in a broad range of industrial applications, the high flammability of many synthetic polymers has limited their use in high fire risk areas [1–3]. Incorporation of flame-retardant (FR) additives into a polymer is the most common approach for enhancing the flame-retardation efficiency [4]. Halogenated compounds are a broad category of FRs extensively investigated due to their high efficiency and low cost [5]. Their use, however, has been restricted recently due to their negative impact on the environment [5]. Halogen-free FRs have been suggested as a more environmentally conscious material for replacing traditional halogenated chemicals [3, 5, 6].

Although FRs vary in their chemical structures, certain general mechanisms of performance enhancement can be attributed to various classes of FRs. For instance, in halogen-free FRs, the prevailing mechanisms can be classified into three categories, namely gas phase dilution, endothermic decomposition, and shield-forming by char formation [7]. There are many efficient halogen-free FRs currently available including phosphorus- and nitrogen-based metal hydrates. Ammonium polyphosphate (APP) is the most well-known FR substance in phosphorus-based class of additives. Moreover, addition of silica aerogels (AG) to polymers can potentially improve flame-retardancy due to the great specific (per weight) mechanical and thermal properties of silica AG [8].

Recently, investigations on the addition of halogen-free FRs to polymeric matrices have triggered substantial and widespread activity in this area. Shi et al. [9] studied thermal conductivity and fire resistance of epoxy composites by incorporating Si_3N_4 and $Al(OH)_3$ (aluminum trihydroxide, ATH) fillers. The results indicated that Si_3N_4 drastically increases thermal conductivity, whereas the ATH has a paramount influence on the flame resistance of epoxy. The incorporation of high loadings (>50%) of these two materials into the epoxy was shown to enhance thermal insulation. The effects of APP and melamine cyanurate (MC) on the flammability and mechanical

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***Corresponding author: Majid Baniassadi,** School of Mechanical Engineering, University of Tehran, Tehran, Iran; and University of Strasbourg, ICube/CNRS, 2 Rue Boussingault, Strasbourg 67000, France, e-mail: m.baniassadi@ut.ac.ir
Ramin Riahipour and Karen Abrinia: School of Mechanical Engineering, University of Tehran, Tehran, Iran
Abolfazl Alizadeh Sahraei: School of Mechanical Engineering, University of Tehran, Tehran, Iran; and Nano Research Laboratory, Allameh Mohaddes Nouri University, Nour, P.O. Box 46415-451, Iran
Nekoda van de Werken and Mehran Tehrani: Department of Mechanical Engineering, University of New Mexico, Albuquerque, NM 87131, USA

properties of the glass fiber reinforced epoxy composites were investigated by Patrick Lim et al. [10], where APP exhibited superior flame-retardancy compared to MC. The limiting oxygen index (LOI) is used as a metric for flammability performance of different materials where in accordance to ASTM D2863, LOI measures the minimum oxygen concentration to support combustion. The higher the LOI value of a material, the less likely it burns. Based on the LOI measurements, it was reported that the addition of only 5 vol% APP exhibited similar self-extinguishing behavior compared to samples containing 20 vol% of MC. Furthermore, 4 vol% APP was shown to have a synergistic effect when added together with 1 vol% MC, on both flame resistance and flexural strength. In another study, Gérard et al. [11] comprehensively investigated the synergistic effect of octa-methyl oligomeric silsesquioxanes (OMPOSS)/APP and carbon nanotube (CNT)/APP on the flammability of an epoxy resin. They reported that CNT provides no improvement on the reaction to fire of the APP/epoxy system. Conversely, addition of the OMPOSS to the APP/epoxy composite made a positive contribution to the fire resistance of the system. Trapping of the degradation gases played a key role in protecting the OMPOSS/APP/epoxy composite against fire.

Ge et al. [8] evaluated hydrophobic and thermal insulation properties of the AG/epoxy composite prepared through a combination of dry mixing and hot press sintering. It was revealed that addition of AG lowers the thermal conductivity in a wide temperature range. Wang et al. [12] determined thermal and FR properties of poly(vinyl alcohol) PVA/clay aerogels with APP and ATH agents. The combination of APP and clay AG had no influence on the onset of polymer decomposition, but a remarkable reduction in the rate of the aerogel decomposition was observed between 250°C and 500°C. Cone calorimeter results demonstrated that both the presence of APP and ATH reduced the peak of heat release rate of PVA/clay composite.

In view of the preceding, there has been an immense effort to achieve advanced epoxy composites with fire resistant properties. The aim of this work is to investigate the effect of silica AG and APP on the thermal, mechanical, and fire resistant properties of the epoxy-based composites.

2 Materials and methods

2.1 Materials

AG with average pore size of 20 nm, porosity of >95%, and density of 0.06 g/cm^3 was supplied by Vaspart Co. Ltd. (Isfahan, Iran). Fine powders of APP (average size of 5 µm, density of 1.98 g/cm^3) were purchased from Pars Idea Chem Co. Ltd., Tehran, Iran. Diglycidyl-ether bisphenol A (Epikote 828) resin and tetra-amine based hardener (HA-11) with a mass ratio of 10:1 were used (Shimi Afsoon Co. Ltd., Tehran, Iran). A 15 wt% reactive diluent, Cardura E10P, existed in the resin.

2.2 Preparation

Composites were prepared using a solution processing method [13]. The samples contained (A) only APP, (B) only AG, or (C) both APP and AG. The volume fractions of fillers in composite types A and B were 0%, 5%, 10% and 20%. For composite type C, the filler contents were 15 vol% (APP:AG volume ratio of 1:2) and 20 vol% (APP:AG volume ratios of 3:1, 1:1 and 1:3). Hereafter, samples are referred to by the volume percentage of each phase followed by the phase name, e.g. sample containing 10 vol% AG and 5 vol% APP is 10AG5APP.

In order to obtain a better dispersion of the constituent materials, the epoxy resin was heated to 50°C to lower its viscosity. Subsequently, adequate volume fractions of AG and APP were added and the mixture was mechanically stirred for 1 h at 2000 rpm. Subsequently, the obtained mixture was degaussed in a vacuum oven at room temperature for 30 min. The hardener (with a weight ratio of 10:1 resin to hardener) was then added and the mixture was mechanically stirred for another 10 min. Finally, the prepared mixture was poured into molds and the whole system was cured in ambient temperature in a vacuum oven for 12 h.

2.3 Characterization

A flame chamber was used to perform the UL-94 (plastics flammability standard) horizontal burning test following the ASTM D 635-10. The anti-dripping and combustion properties of the composites were extracted primarily from this test. The standard samples for UL-94 were fabricated to dimensions of $100\times12\times2$ mm^3. The LOI values were measured using an HC-2 oxygen index meter (Jiangning Co, China), according to the ASTM D 2863 with a sample size of $130\times6.5\times3.2$ mm^3. The decomposition behavior and thermal stability of the composites were quantified by thermo-gravimetric analysis (TG/DTA 6300, SII Nanotechnology, Japan). TGA was performed in air at a heating rate of 10°C/min from room temperature to 700°C following the ASTM E 1131. Differential scanning calorimetry (DSC, 2000 FC by Netzsch Co., Germany) and dynamic mechanical analysis (DMA, Q800 by TA Instruments, USA) were used to evaluate the influence of FR additives on the glass transition temperature (T_g) and mechanical performance of the composites. In accordance with ASTM D7028-07, the DMA test specimens had a span to thickness ratio of >10. Tests were performed at a frequency of 1 Hz, strain amplitude of 0.1%, heating rate of 5°C/min, and temperature range of approximately 30°C–120°C. For DSC, 10 mg of each sample was heated from ambient temperature to 300°C at a heating rate of 10°C/min under a nitrogen flow (ASTM D 3418). The average values of the measured properties for a minimum of five different samples were reported for each composite to ensure reproducibility and accuracy.

Thermal conductivity of the samples was measured using a discovery DXF-200 flash diffusivity system (TA instruments, USA). Tablets with a diameter of 1.27 and a thickness of 1–2 mm were cut from the samples. Xenon flash induces a uniform heat pulse through the sample if it is opaque. Samples in this study were translucent, thus a graphite spray coat (Rust-Oleum graphite spray) was applied to one side of the sample. The comparative mode of the DXF-200 was used to simultaneously measure the specific heat and thermal diffusivity of the samples. In this measurement the flash method is simultaneously applied to a reference (Austenite stainless steel in this study) and an unknown sample where identical flash power and thermal conditions are applied to both samples. By definition, thermal conductivity was then calculated from the following equation:

$$\lambda = \alpha \rho C_p \tag{1}$$

where λ is the thermal conductivity, α is the thermal diffusivity, ρ is the density, and C_p is the specific heat. Density was calculated manually by measuring the mass (Nevada Radwag scale, USA: 0.0001 g) and volume (dimensions were measured using a Mitutoyo Caliper, USA: 0.1 microns) of a rectangular sample.

An FEI Q3D scanning electron microscope (SEM, Zeiss, Germany) was used to acquire micrographs of samples. For SEM imaging, samples were immersed in LN2, fractured immediately after, and their fractured surfaces were coated with 4 nm of carbon.

3 Results and discussion

3.1 Morphology

Representative SEM images of the fractured surface of the different samples are shown in Figure 1. Distribution of APP in 20APP/epoxy composite is shown in Figure 1B. Although larger sized APP particles are observed in the micrograph, APP is still homogenously dispersed in the epoxy matrix. The SEM micrograph of the 20AG/epoxy composite (Figure 1C) shows that AG particles are engulfed and encapsulated in the matrix. This is because AGs are composed of an interconnected network of channels. Furthermore, compared to the 20APP sample, some large pores are visible on the surface of the 20AG composite. These pores are the origin of dropping mechanical and physical properties of the composites. Morphology of the sample containing APP and AG is characterized in Figure 1D (5AG15APP). A close observation reveals that there are no considerable differences in the dispersion degree of the constituent materials, compared to the sample containing APP or AG alone.

3.2 Thermal properties

Table 1 summarizes the results of UL-94 test, i.e. burning length, burning time, and burning rate. Only the neat epoxy samples exhibited dripping without significant formation of char, while the addition of AG and/or APP eliminates dripping for the duration of the experiment. In general, dripping of flaming polymer during combustion promotes the progression of fire [14]. On the contrary, formation of stable surface layer of char blocks further ignition by limiting the heat and mass transfer from the flame to the polymer and from the polymer to the flame, respectively [14].

The addition of AG to the epoxy matrix decreases the burning rate of the epoxy, however, AG loading in excess of 10 vol% has no considerable effect on the combustion rate of the composites. The flammability resistance of the composite shows dramatic improvement when infused with APP. For the 5APP sample, flame extinguished within the first 25 mm, while in 10APP and 20APP samples no flame was produced in atmospheric conditions. The APP/AG/epoxy composites with 10 vol% APP or higher also did not burn in the horizontal burning test. Lastly, the 5APP system with the addition of 10 vol% of AG shows a reduction on the burning time from 30 to 17 s.

In order to investigate the effect of APP and AG addition on the epoxy composite, the 20APP and 15APP5AG samples were examined under a modified burning procedure. In this experiment, the sample was positioned horizontally above a 7 cm flame for 60 s and subsequently examined. As shown in Figure 2, the addition of 5 vol% AG results in a noticeable reduction of charring on the

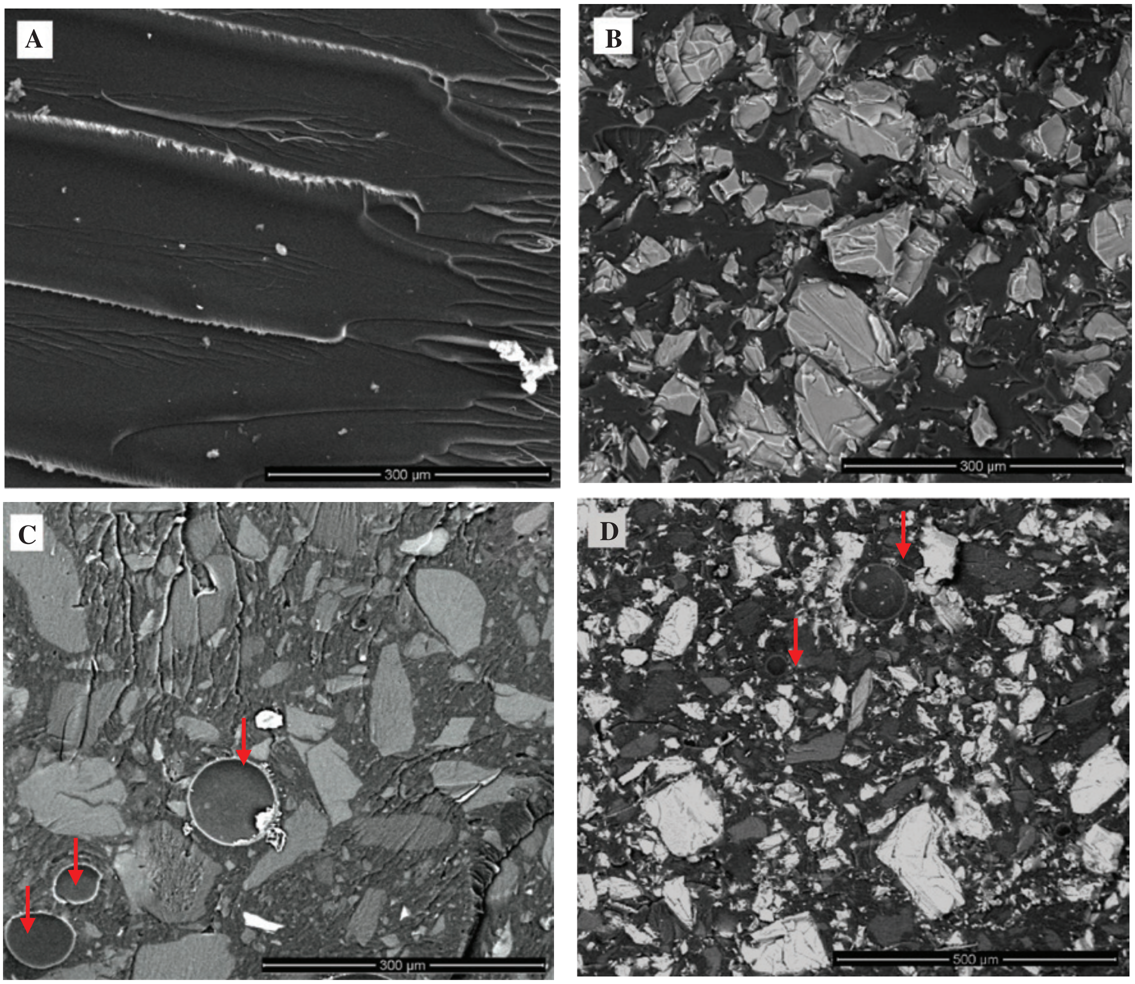

Figure 1: Representative SEM micrographs of the: (A) neat epoxy, (B) 20APP, (C) 20AG and (D) 5AG15APP samples showing effective dispersion of AG and APP phases.

Table 1: Characterization of flame-retardancy of the epoxy composites.

Sample	Flame reaches 25 mm mark	Burning length (mm)	Burning time (s)	Burning rate (mm/min)	LOI (%)
EP	Yes	100	160	37.5	20.2
5AG	Yes	100	249	24.1	23
10AG	Yes	100	314	19.1	24.1
20AG	Yes	100	321	18.7	24.3
5APP	No	18	30	–	26.8
10APP	No	0	–	–	29.3
20APP	No	0	–	–	41
5APP10AG	No	13	17	–	27.3
10APP10AG	No	0	–	–	29.6
5APP15AG	No	0	–	–	27
15APP5AG	No	0	–	–	38.6

surface of the sample. These carbonaceous chars seem to retard the heat transfer and substantially improve the flammability properties of the fabricated composites. Also it seems that the existence of AG in the composite leads the flame toward the edges of the sample, thus lowering the internal sample degradation. This phenomenon is most probably ascribed to the excellent thermal insulation properties of AG.

Figure 2: The char residue in: (A) 20APP and (B) 15APP5AG.

To better understand the combined effect of the fillers, the LOI of the samples was measured. The LOI with respect to various filler concentrations is presented in Table 1. Neat epoxy, with the LOI value of 20.2%, is easily combustible in atmospheric condition. With the addition of 5 vol% and 10 vol% AG, the LOI value slightly increases to 23% and 24.1%, respectively. Further increase in the AG above 10 vol% did not improve the LOI. A material must have a minimum LOI of 26% in order to be categorized as self-extinguishing [10, 15]; the addition of the AG did not make the composite self-extinguishing. Compared with epoxy composites containing only AG, the LOI values of the APP/epoxy composites show substantial improvement. The LOI values increase dramatically with increasing concentration of APP up to 20 vol%, where the LOI reaches a maximum of 41%. It is therefore clear that APP is more capable of improving self-extinguishing behavior in epoxy, especially at higher loadings.

Investigation of the LOI data of the APP/AG/epoxy composites provides some interesting insight into the trends associated with various filler ratios. At a constant concentration of AG (10 vol%), increasing APP loading increases the LOI. Conversely, at 10 vol% APP, the addition of AG has no effect on the LOI. A slight decrease of LOI is observed for the 5APP15AG sample compared with the 5APP10AG. This is likely due to difficulty in dispersion of AG in epoxy matrix at higher loadings. The 5AG15APP exhibited a large LOI of 38.6%.

Figure 3 shows TGA and differential thermal analysis (DTA) profiles for the different samples. The primary results of Figure 3 are summarized in Table 2. Three temperatures are extracted from TG curves: (1) T_5, which demonstrates the temperature of a small weight loss of 5%, (2) $T_{\max}$, exhibits the temperature at which the maximum weight loss rate occurs, and (3) T_f, temperature at which constant residual weight of sample is achieved. T_5 also represents apparent thermal stability of composites [16]. The initial mass loss below 150°C is due to the possible evaporation of the absorbed water and the remaining reactive diluent (Cardura E10P) [16]. The possible monomeric compounds remaining from the incomplete polymerization of the epoxy is also evaporated below 150°C. The T_5 of the 20APP sample is 186°C, which is about 21°C lower than that of the neat epoxy. Addition of 5 vol% AG in the 15APP5AG system increases T_5 to 202°C. In line with this

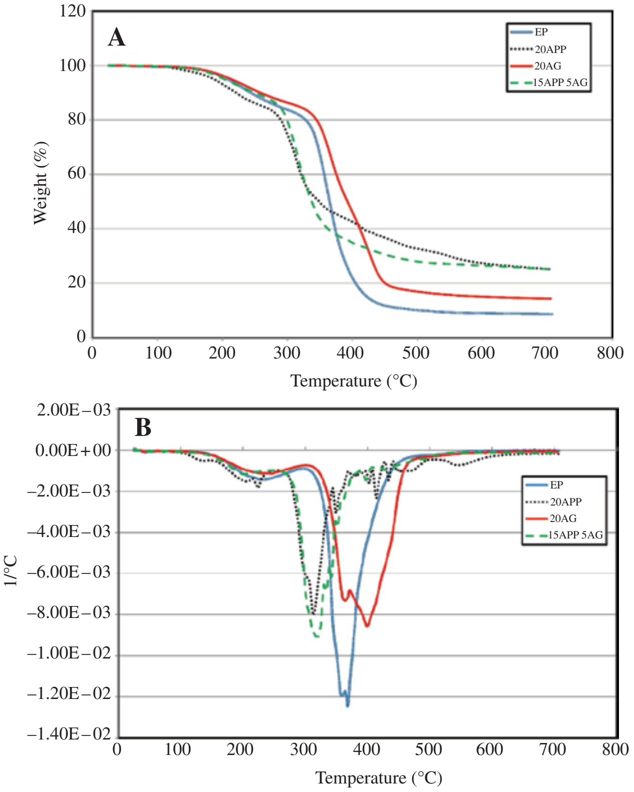

Figure 3: TG and DT curves of the neat epoxy, 20APP, 20AG and 15APP5AG.

Table 2: TGA data of neat epoxy and epoxy composites.

Sample	T_5 (°C)	T_{max} (°C)	T_f (°C)	Residue (%)
EP	207	368	450	8.63
20AG	213	395	470	14.3
20APP	186	313	580	25.09
15APP5AG	202	315	520	25.15

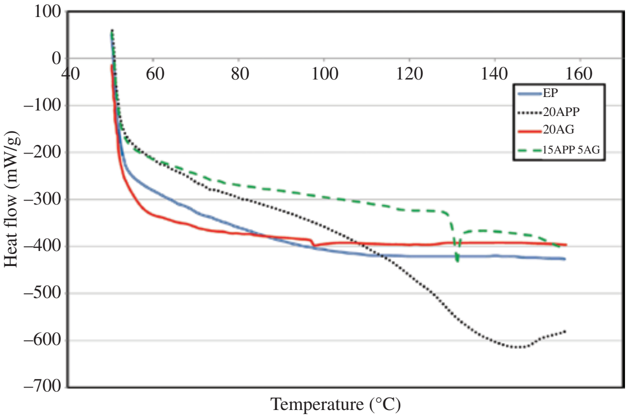

Figure 4: DSC curves of different samples.

Table 3: T_g values from the DSC method.

EP	10AG	20AG	10APP	20APP	5AG15APP
66.3	74.2	66.1	68.3	67.9	69.4

trend, 20AG sample shows a 6°C increase in T_5 over the neat epoxy. It can be concluded that the addition of APP decreases the initial thermal stability of epoxy, while AG can slightly improve it. In fact, the presence of AG particles in the epoxy can be associated to hinder the evolution of volatile decomposition substances from the epoxy matrix [14, 17].

In neat epoxy, T_{max} occurs at 368°C. Addition of 20 vol% AG increases the T_{max} to 395°C. Moreover, total weight loss percentages for the neat epoxy and 20AG composite between 250°C and 450°C, are 78% and 70%, respectively. Accordingly, it is unambiguous that the presence of AG leads to major delay in thermo-degradation of epoxy due to physical barrier preventing of AG particles. With the addition of 20 vol% APP, T_{max} is sharply reduced to 313°C. In this case, the decomposition rate is also decreased, which facilitates the formation of heat-resistant char [18, 19]. The underlying mechanism of thermal degradation of APP/polymer composites has been comprehensively investigated in the literature [17, 20, 21]. As a brief explanation, chemical reactions of APP and epoxy resin lead to formation of phosphorous-rich layer, resulting in the lower degradation temperature and decomposition rate of APP/epoxy composites. At higher temperatures, the protective layer decomposes to form a compact char coating surface, which enhances the thermal stability of APP/epoxy composite over 450°C [20]. The remaining char of 20AG, 20APP and 15APP5AG samples is respectively ~6%, ~17% and ~17% higher than the neat epoxy. This residual char is a useful indicator for forecasting fire retardancy of the materials. The APP remarkably improves the char-forming behavior.

The T_f is evidently increased in the composites containing APP as the FR. Based on the results, one can conclude that addition of APP to the epoxy matrix results in a much better thermal performance at higher temperatures compared to the AG and neat epoxy samples. The AG integrated with APP, however, shows effective FR efficiency in epoxy matrix.

Incorporation of APP and AG in the epoxy matrix also affects its glass transition temperature (T_g). Using DSC (Figure 4), the extracted T_g values for the different samples are summarized in Table 3. The T_g of the reference neat epoxy is 66°C. When 10 vol% AG is incorporated into the epoxy matrix, T_g increases to 74°C. The observed increase is ascribed to well-dispersed AG particles in the matrix. In fact, improving dispersion uniformity of additives can hinder the segmental movements of cross-linked epoxy matrix, hence the increase in T_g [22]. Conversely, at higher volume fractions of fillers, increase in interactions between the monomers and fillers during the polymerization process leads to the reduction in the degree of crosslinking. Therefore, a drop in T_g is expected

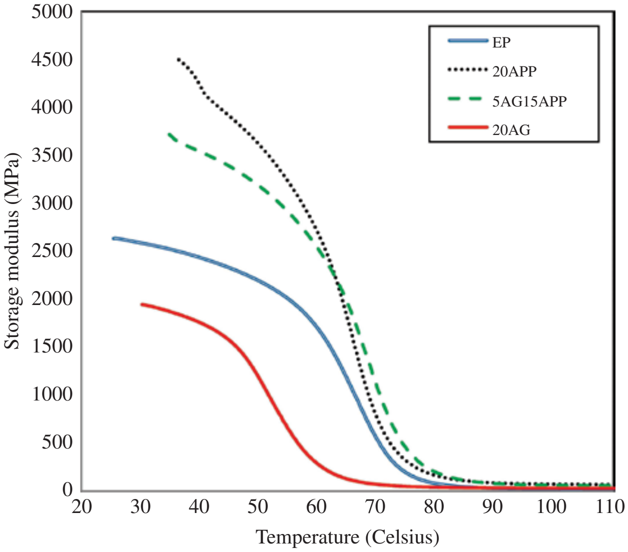

Figure 5: Temperature-dependent storage modulus for different samples.

Table 4: Thermal properties of neat epoxy and its composites.

Sample	Density (kg/m^3)	Specific heat ($J/kg\cdot K$)	Thermal diffusivity (mm^2/s)	Thermal conductivity ($w/m\cdot K$)
Epoxy	1134.0	2490.2	0.092	0.260
20AG	1025.0	2517.5	0.123	0.317
20APP	1201.6	2700.7	0.173	0.561
5AG15APP	1194.9	2047.4	0.150	0.367

[22, 23]. For the 20AG, the T_g decreases to the T_g of neat epoxy. A slight decrease in T_g is also observed in the 20APP composite compared to the 10APP sample. Szolnoki et al. [22] reported significant improvement in T_g of the APP/epoxy composites due to the addition of small amounts of APP. The addition of AG to the APP/epoxy system also resulted in increase in the T_g. These results authenticate the synergistic effect of the APP and AG on the T_g of the epoxy composites.

As shown in Figure 5, storage modulus at different temperatures for the 20AG sample decreases compared to the neat epoxy sample and increases for the 20APP sample. As expected, the highly porous AG particles deteriorate the mechanical performance of the epoxy. The net effect of APP and AG additions to the next epoxy in the 5AG15APP sample results in an overall improvement in the performance over the neat epoxy sample. It is evident from the DMA curves that the transition to a rubbery state for both the 20APP and 5AG15APP samples occurs at a relatively higher temperature compared with the neat and 20AG samples.

Density, thermal diffusivity, specific heat, and the calculated thermal conductivity values for the different samples are summarized in Table 4. In general, the addition of APP and AG increases the thermal conductivity. Addition of 20 vol% AG to epoxy increases the thermal conductivity by only 20%, while the addition of 20 vol% APP increases it by 115%. This could be explained by the structural differences between the APP- and AG-based composites where AG contains pores and therefore has a much smaller thermal conductivity compared with APP. Interestingly, combining AG and APP in the 5AG15APP sample only increased the thermal conductivity by 40%. This can be responsible for the burning behavior of the 5AG15APP sample where the insulating properties of the AG hinder heat transfer to the bulk epoxy.

Using the rule of mixture a density of 590 kg/m^3 is calculated for the AG phase in the 20AG sample. This value is much larger than the density of AG itself (~60 kg/m^3). It is therefore concluded that AG particles are partially infused by the epoxy. As a result, although it was expected that addition of AG lowers the thermal conductivity of the base epoxy, it slightly increased it.

4 Conclusions

In this study, the individual and combined effects of utilizing AG and APP on the fire resistant and thermal properties of the Epikote 828 epoxy were investigated. At the same filler loading, the flammability resistance of the epoxy was improved to a higher degree by the addition of APP compared with the AG. The 20APP and 15APP5AG samples showed the highest value of LOI among all the tested samples. The results also indicated that only 5 vol% APP is needed to attain self-extinguishing behavior in this epoxy system. The incorporation of APP into the epoxy improved the thermal stability and mechanical properties at higher temperatures. Similarly, the APP addition significantly improved the char formation. The sample with 15 vol% APP and 5 vol% AG, however, yielded the highest amount of char formation. It was concluded that replacing 5 vol% of APP in the 20 APP sample with 5 vol% of AG can improve the T_g and reduce the density, while no apparent difference in FR properties of these two samples was observed.

Funding: This study was funded by The Iran National Science Foundation (INSF).

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