

The Effect of Ammonium Polyphosphate and Nanoclay on the Rheological, Thermal, and Flame Retardant Properties of Epoxy

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ABSTRACT

The effect of ammonium polyphosphate and nanoclay on the rheological and flame retardant properties of epoxy is evaluated. Epoxy was filled with long chain ammonium polyphosphate and nanoclay and the kinematic viscosities of the mixtures with different amounts of filler were measured at 40°C using a viscosity flow cup. The epoxy composites were subsequently casted to form cylinder-shaped specimens and their flame retardant properties were evaluated by a cone calorimeter at a heat flux of 50 kW/m². Furthermore, thermal properties of the epoxy specimens were determined using thermogravimetric analyzer and differential scanning calorimeter and these results are discussed.

INTRODUCTION

Flame retardants are used in polymers to increase the ignition time, improve the self-extinguishability, decrease the heat release rate during combustion, prevent the formation of flammable drops, and lower the formation of smoke and toxic gases. The most commonly used halogen-based flame retardants are believed to be one source for the increased formation of smoke as well as toxic, corrosive and/or carcinogenic gases during fire^{1,2}. Due to the increasing interest in the environmental issues and more stringent safety standards, new non-halogenated possibilities are widely

explored³. The flame retardants in the future should be cost-effective, environmentally-friendly, and effective in low amounts. Furthermore, they should not degrade during burning, processing or use, or affect the processing or the mechanical properties of the product.

The drawback of traditional non-halogenated flame retardants, such as phosphorus-based compounds and metal hydroxides, is the fact that higher filler contents are needed to obtain similar fire performance than with the halogenated compounds¹. Disadvantages of high loading levels are high density, lack of flexibility and poor mechanical properties of the final products as well as problematic compounding due to the increased resin viscosity⁴. Since the halogenated compounds are slowly being replaced by more environmentally-friendly additives, the latest research trends mostly focus on the development on new combinations of traditional halogen-free flame retardant additives and totally new materials, such as nanoparticles. Nanometric particles are reported to improve thermal, mechanical, and physical properties of polymers⁴, but they do not solely serve adequate fire resistance to meet the required standards¹. Their combination with traditional flame retardants, however, is an interesting approach and also recently studied^{1,5}.

The objective of this work was to study the effect of traditional ammonium

polyphosphate (APP) on the rheological, thermal, and flame retardant properties of epoxy as well as to examine the possible synergy between APP and nanoclay.

EXPERIMENTAL

Materials used

In this study, a commercial epoxy resin, namely Epikote 232 was used in combination with amine blend curing agent, namely TB-B561 (both supplied by A. Graveolens Oy). Surface treated long-chain ammonium polyphosphate (FR CROS 486) was supplied by Budenheim and the onium ion modified nanoclay (Nanomer I.30E) by Nanocor. The amount of APP in the matrix varied from 10 to 40 wt.% while the nanoclay content was kept constant (3 wt.%).

Sample preparation

The epoxy specimens were prepared using mechanical and ultrasonic mixing combined with heating (40°C) in order to enhance the dispersion of the particulate fillers to the matrix. After two hours of mixing, the hardener was added to the epoxy resin and the mixture was placed under vacuum to remove the excess air from the matrix. Cylinder-shaped (\varnothing 80 mm) samples with a thickness of approximately 6 mm were subsequently manufactured by pouring the mixture to aluminum mould cavities for curing and vacuumed once more. Finally, epoxy composites were cured in an oven for 2 hours at 80°C with 30 minutes heating and cooling ramps. Prior manufacturing, the fillers were oven-dried at 80°C for several hours.

Characterization methods

In order to measure the kinematic viscosities of the liquid epoxy samples, a 120-ml batch of the filler doped epoxy resin was manufactured as described above. Kinematic viscosities were measured immediately after the addition of the curing agent using a viscosity flow cup (Erichsen

GmbH & Co., Model 243/II/4). Tests were done at 40°C according to ISO 2431.

The fire behaviour of the epoxy composites were evaluated using a cone calorimeter (Fire Testing Technology) according to the test procedure described in ISO 5660. Cone calorimeter experiments allow the evaluation of, for example, heat release rate (HRR), peak heat release rate (PHRR), total heat released (THR), and total smoke produced (TSP). Heat flux of 50 kW/m² was applied and two to three parallel tests were done. Samples were tested in a horizontal position.

Thermogravimetric (TGA) experiments were carried out using a Perkin Elmer Pyris TGA 6 instrument under oxygen with a heating rate of 10°C/min from 30°C to 1000°C. Furthermore, glass transition temperatures (T_g) of the epoxy samples were examined with a differential scanning calorimeter (Netzsch DSC 204 F1). The heating-cooling cycle was repeated two times to evaluate the success of the curing reaction of the epoxy resin. The heating cycles were recorded from 25°C to 250°C at a scanning rate of 10°C/min under nitrogen flow (50 ml/min).

RESULTS AND DISCUSSION

Rheological and flame retardant properties

Table 1 shows that the kinematic viscosities of the liquid epoxy mixtures increase almost linearly as the APP content in the matrix increases. In fact, the kinematic viscosity of the epoxy sample with 40 wt.% of APP is over four times higher compared to pure epoxy. At the same time it obtains the lowest PHRR and THR values as suggested by the cone calorimeter experiments. The improved fire retardant properties of the APP composites can be explained by the fact that APP acts as an intumescent and forms an insulating gas layer on the top of the material during fire. This layer reduces the heat transfer between the polymer sample and the heat source and limits the oxygen diffusion into

Table 1. Rheological and flame retardant properties of epoxy samples

Sample	Kinematic viscosity in 40°C (mm ² /s)	PHRR (kW/m ²)	THR (MJ/m ²)	TSP (m ²)
EP	27	1222	159	25
EP + 10 wt.% APP	34	934	116	17
EP + 20 wt.% APP	49	879	105	13
EP + 30 wt.% APP	65	494	85	11
EP + 40 wt.% APP	118	225	55	8
EP + 3 wt.% I.30E	33	1274	154	25
EP + 10 wt.% APP + 3 wt.% I.30E	51	485	123	19
EP + 20 wt.% APP + 3 wt.% I.30E	61	363	92	10

the material¹. Fig. 1 shows the reference sample and the sample with 30 wt.% of APP during cone calorimeter test. The formation of protective carbonaceous char on the surface of the sample EP + 30 wt.% APP is apparent. The amount of char in the residue increased as the APP content in the matrix increased as expected. Intumescent char is known to act as a physical barrier in preventing the formation of smoke in the underlying material⁶. Our results agree with that since less smoke was produced during the fire when APP is incorporated into the epoxy matrix.

Even if the application of APP looks promising in terms of fire resistance it must be taken into consideration that high resin viscosities cause problems in the manufacturing and weaken the mechanical properties. Thus a balance between improved flame retardant properties and

viscosity is crucial. Therefore, a combination of nanofillers with traditional flame retardants is an attractive approach to reduce the amount of APP and minimize the undesired viscosity increase.

At first, the effect of sole addition of nanoclay on the flame retardant properties of epoxy was studied. Although it has been widely reported^{1,5,7-9} that a small amount of nanoclay decreases the PHRR value of several polymeric materials, such behaviour could not be seen in our results. On the other hand, the combination of APP and nanoclay showed a clear synergistic effect by reducing the PHRR value significantly compared to the neat epoxy and epoxy/APP composites: with the sample EP + 20 wt.% APP + 3 wt.% I.30E the PHRR value decreased 70% compared to the neat epoxy while the decrease was only 28% with the sample EP + 20 wt.%

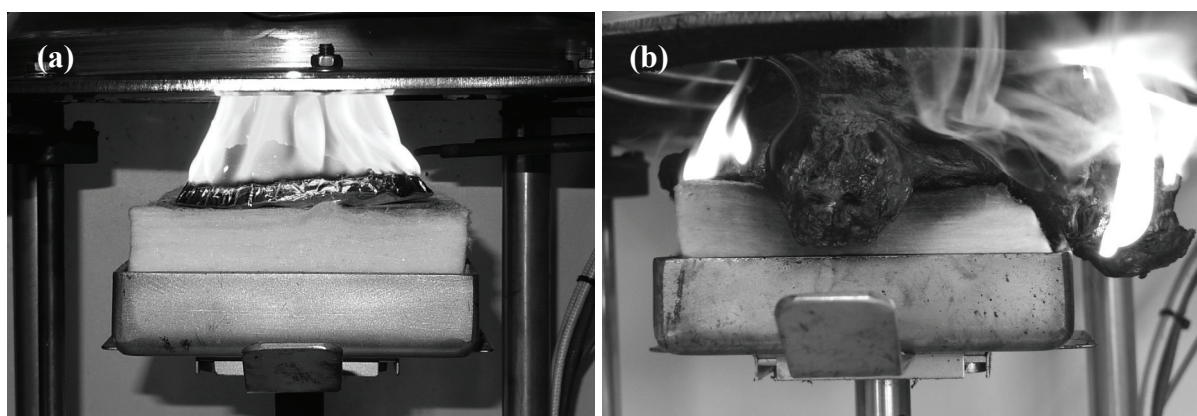


Figure 1. (a) Pure epoxy and (b) sample EP + 30 wt.% APP during the cone calorimeter test.

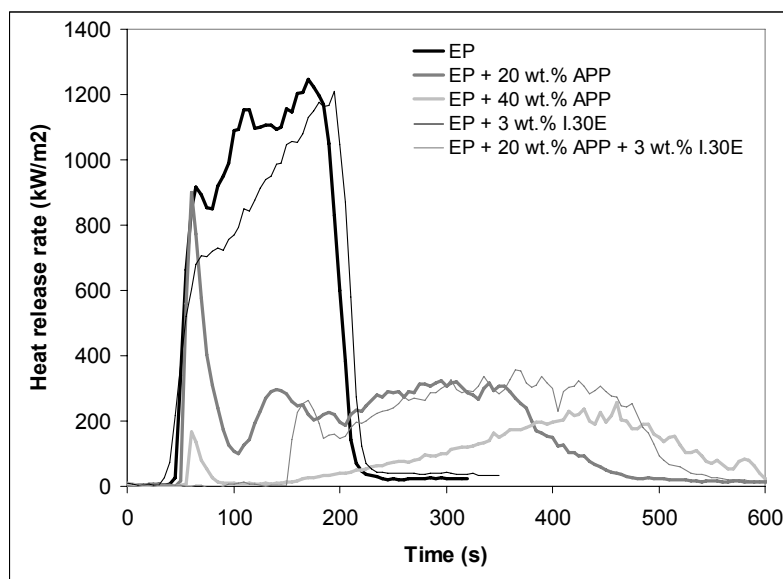


Figure 2. Heat release rates of selected epoxy/APP/I.30E composites.

APP. In addition to the decreased PHRR values, the combination of 20 wt.% APP and 3 wt.% of nanoclay delayed the ignition time of the epoxy for over two minutes compared to the other samples. THR did not significantly change upon nanoclay addition, which is an indication of slow but complete burning of nanocomposites⁹. Examples of heat release rate curves of the selected samples are presented in Fig. 2. However, it was noted during manufacturing that the gel-time of epoxy mixtures was significantly decreased when nanoclay was added to the matrix. This behaviour has also been observed by Román et al., who noticed that the onium ion of the modified nanoclay catalyses the curing reaction of epoxy¹⁰. Therefore, it can be stated that the increased viscosity values of the nanoclay samples are mainly caused by the accelerated curing.

Thermal properties

TGA experiments give important information about the decomposition process although care must be taken in their direct application to materials fire behaviour². TGA results (Fig. 3) show that APP samples show a decrease in thermal stability at the temperature range from 300 to 360°C, but a clear increase at

temperatures over 360°C. Thermal degradation of pure APP has already been described in the literature^{2,12}. In the first degradation stage, starting at about 300°C, ammonia and water are released¹². The resulting degradation products crosslink in polyphosphoric acid and a protective phosphorus-rich char layer is formed on the top of the material^{11,12}. In second stage, starting at about 550°C, an evolution of polyphosphoric acid and/or its dehydration to P₄O₁₀ has been suggested¹². Small amount of nanoclay, on the other hand, does not have a significant effect on the thermal degradation of epoxy, in agreement with the results from Zhang et al.⁸.

DSC experiment results (Table 2) suggest that the glass transition temperature values (T_g) of the samples are not significantly decreased although a relatively high amount of APP is introduced to the matrix. This implies that APP does not interfere with the crosslinking of the epoxy resin. The more pronounced effect of nanoclay on the T_g values is probably attributed to its above mentioned catalytic effect in the epoxy matrix. According to Lan et al., clay can promote a self-polymerization reaction in epoxy systems¹³. It should be thus noted that if a

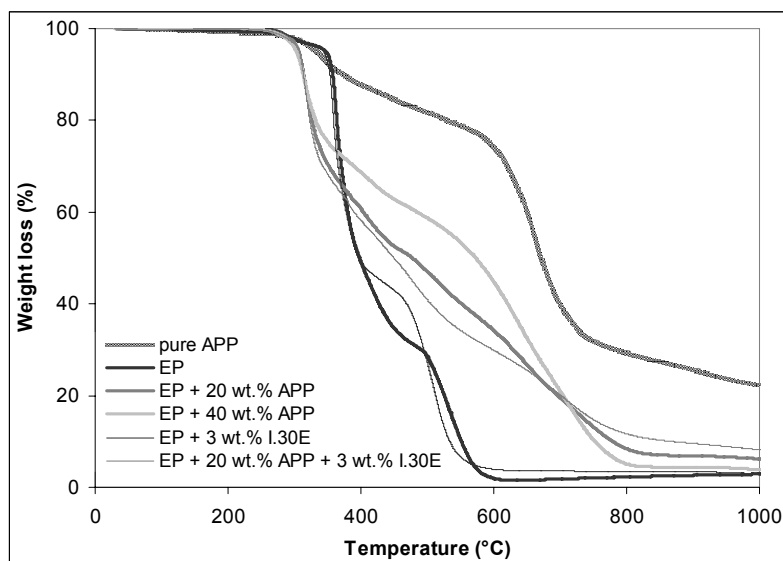


Figure 3. TGA-curves of selected epoxy/APP/I.30E composites.

significant part of the epoxy curing reaction occurs via self-polymerization catalyzed by the onium ion of the clay, then there is excess amine for the epoxy groups and the reaction will be off stoichiometric¹⁰. According to Román et al., one effect of this kind of behaviour is the reduction of the glass transition temperature¹⁰, which agrees with our results.

CONCLUSIONS

Epoxy samples with ammonium polyphosphate and nanoclay were successfully manufactured. APP was shown to improve the flame retardancy of epoxy, but it also drastically increased the kinematic viscosity of the epoxy resin in higher filler contents. A synergistic effect on

flame retardant properties was achieved by the combination of ammonium polyphosphate and nanoclay resulting reduced PHRR value compared to the neat epoxy and epoxy/APP composites. Furthermore, the ignition time with 20 wt.% of APP and 3 wt.% of nanoclay was notably delayed compared to the other samples. It was noticed, however, that the onium ion modified nanoclay accelerates the curing of the epoxy and further increases the kinematic viscosity of the resin. This behaviour was also supported by the fact that glass transition temperature values of the nanoclay composites were clearly decreased compared to the neat epoxy. Thus the measured viscosity

Table 2. Glass transition values of selected epoxy/APP/I.30E composites.

Sample	T _g (°C) 1 st heating	T _g (°C) 2 nd heating
EP	83	85
EP + 10 wt.% APP	80	82
EP + 20 wt.% APP	77	83
EP + 30 wt.% APP	78	84
EP + 40 wt.% APP	79	86
EP + 3 wt.% I.30E	74	79
EP + 10 wt.% APP + 3 wt.% I.30E	72	78
EP + 20 wt.% APP + 3 wt.% I.30E	72	80

increase of the resin was partially caused by this catalytic effect.

In summary, it was proved that by the combination of APP and nanoclay, improved flame retardant properties were obtained with lower filler contents.

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