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The Effect of Nanometals on the Flammability and Thermooxidative Degradation of Polymer Materials

A Antonov [a], M. Yablokova [a], L. Costa [b], A. Balabanovich [c], G. Levchik [c] & S. Levchik [c]

[a] Institute for Synthetic Polymeric Materials, Profsoyuznaya 70, Moscow, RUSSIA

[b] Dipartimento IFM, Universita di Torino, Via P. Giuria 7, Torino, 10125, ITALY

[c] Research Institute for Physical Chemical Problems of Belaruassian University, Leningradskaya 14, Minsk, 220080, BELARUS

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[a]*Institute for Synthetic Polymeric Materials, Profsoyuznaya 70, Moscow, RUSSIA,* [b]*Dipartimento IFM, Universita di Torino, Via P. Giuria 7, Torino, 10125, ITALY and* [c]*Research Institute for Physical Chemical Problems of Belaruassian University, Leningradskaya 14, Minsk, 220080, BELARUS*

It was found that finely dispersed metals (nanometals) at low addition (≤1% wt.) increase flammability of neat polypropylene in spite of strong enhancement of char yield. The nanometals do not seriously affect flammability of neat epoxy resins. On the other hand, it was shown that the nanometals are very efficient co-additives in combination with some phosphorus containing fire retardants in both polypropylene (thermoplastic) and epoxy resin (thermoset). At the specific content of the metals, a sharp maximum is observed on the dependence of oxygen index on concentration of fire retardant additives which proves occurrence of strong synergistic effect. Thermal analysis and characterization of solid residues allowed to approach to the mode of fire retardant action of the nanometals..

Keywords: nanometals; fire retardants; polymer; char formation; thermal degradation

Epoxy resins (ER) are widely used in electronic, instrumental and automotive industries. ER combine high thermal stability with high adhesion and good dielectric properties. Upon curing, ER cross-links producing three dimensional polymeric network. The thermal oxidative degradation of ER results in the formation of some char.

We studied the effect of nanoparticles (NPM) metals on the flammability of ER and found that the addition of NPM metals (content 0,05 - 1 %) does not

affect the flammability. Oxygen index (OI) does not change upon increasing of NPM metals content.

On the other hand, NPM metals becomes very efficient in ER fire retarded with ammonium polyphosphate (APP). In this case, the performance of the NPM strongly depends on the metal content in the formulations (fig.1). The maximum efficiency is achieved at NPM Cu content of 0.1 %, e.g. OI increases from 31 for ER + APP to 37 for ER + APP + NPM Cu.

The effect of NPM Cu on the thermal behavior of ER was accessed by the thermal analysis. As shown by DSC and thermogravimetry results, NPM Cu does not interfere with the thermal decomposition of APP below 300°C. Therefore, we assume that no chemical reaction between APP and Cu occurs in this temperature range. On the other hand, NPM Cu significantly affects the thermal degradation of APP, ER and ER+APP mixture (fig.2). The addition of NPM Cu results in increasing the rate of decomposition of the formulation in the high temperature range. On the other hand, NPM Cu accelerates the rate of char formation in the terms that the char is formed at lower temperature in the presence of Cu. With this we can suggest that the

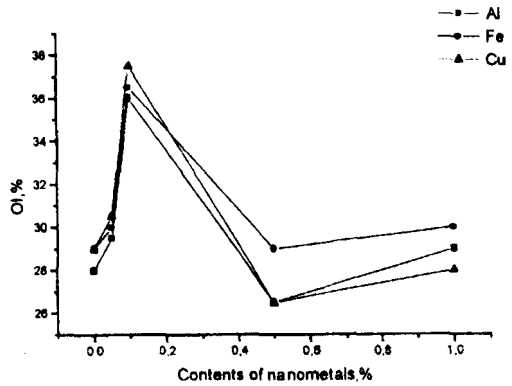

Fig.1 The data LOI composition on based of epoxy resin with 15% mass. APP for various contents nanometals.

Fig. 1. The data LOI composition on based of epoxy resin with 15% mass. APP for various contents of nanometals

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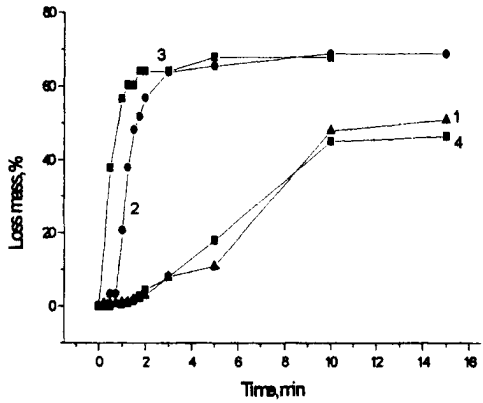

Fig.2.The data of isothermal decomposition of epoxy ammonium polyphosphate (APP). N1-ER+15%APP+1%Cu; N2-ER+1% Cu; N3-ER; N4- ER+15%APP

mixture of ER+APP+Cu burns faster than ER+APP in the first moment, but then the char is formed and the polymer extinguishes.

It is very interesting that the content of NPM Cu affects the rate polymer decomposition (fig.3).

Solid residues of the thermal degradation of ERs containing APP and NPM Cu have been characterized by FTIR. It was found that in the presence of NPM Cu more phenols are produced compared to the ER + APP formulation. Furthermore, IR spectroscopic data showed that Cu facilitates interaction between APP and alcohol groups existing in the cured ER. After further heating, Cu accelerates decomposition of the phosphoric esters formed and helps to volatilization and cross-linking of the aliphatic part of ER. We suggest that in the presence of Cu the formation of cross-linked thermally stable structure occurs faster than in the absence of the nanometal

It is known that the efficiency of the intumescent fire retardant systems based on APP depends on the kinetics of the foamed char formation and its mechanical strength. In this work we investigated the kinetics of the char

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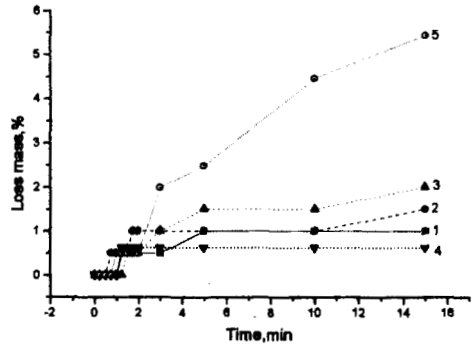

Fig.3 The data of isothermal decomposition of ammonium polyphosphate (APP) and high density Cu. Content of high dispersity Cu, %mass : 1-0 ; 2-0.05 ; 3-0.1 ; 4-0.5 ; 5-1

foaming during degradation of ER+APP and ER+APP+Cu and the mechanical strength of the chars. It was shown that Cu lowers down the temperature interval of the char formation (fig.4). Furthermore, the volume of foaming is higher for ER+APP+Cu than that for ER+APP. The addition of Cu nanoparticles results in improving the mechanical strength of the char.

Table 1. The effect of nanometals on the flammability of PP.

Metal	Content, % mass	Size of particles	OI
Cu	0.005-1	3-50 nm	14.5
Cu	0.005-1	10-100 mkm	16.5
Cu	0.005-1	> 200 mkm	17.7
Al	0.005-1	3-50 nm	15.5
Fe	0.005-1	3-50 nm	15.5
Ni	0.005-1	3-50 nm	17.5

Thus, we conclude that NPM Cu interferes in the thermal decomposition mechanism of ER+APP. NPM Cu increases the rate of char formation and benefits to the mechanical strength of the char.

Polypropylenes– are industrial thermoplastic materials which are widely used for development of commercial, technical and household products. The effect of

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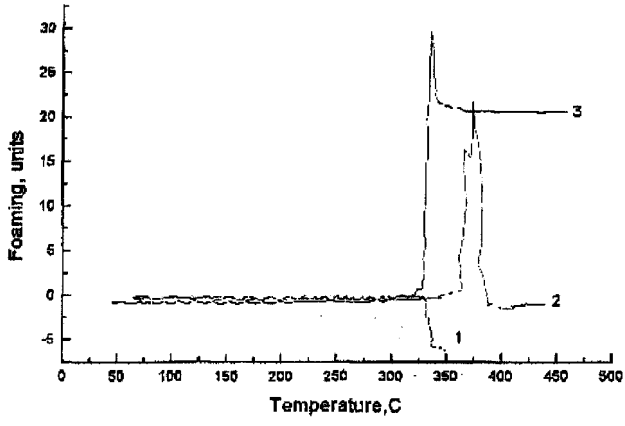

Fig.4. The data of foaming composition on based of epoxy resin with 15% mass. Intumescent systems: 1- with absent IS, 2- APP, 3- APP+0.1% Cu.

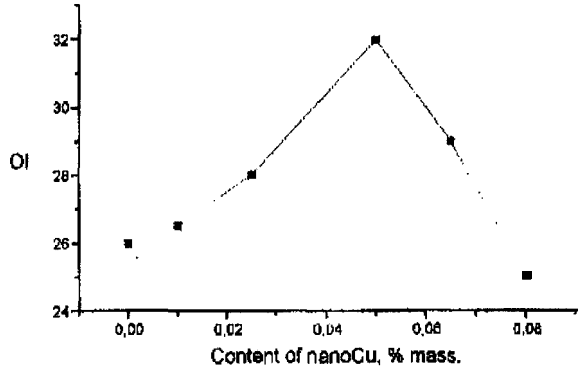

Fig.5 The OI data for PP+APP/PER (7:3, 20 % mass.)

NPM Cu on the flammability of PP have been studied (Table 1). As can be seen from Table 1 metals decrease in the OI of PP, NPM Cu increase flammability of neat PP at 0.005-1.0 % wt. loading, the OI of PP decreases from 17.5 to 14.5. In the case of PP, the NPM Cu prevents flaming drips appearance and cause charring of the polymer, which does not char in the absence of the additives. Apparently the NPM Cu with higher specific surface are more effective in

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increasing the char formation, but formed char can not prevent the polymer surface from heating flow and the flammability of PP increasing.

The effect of NPM Cu on the efficiency of APP along with pentaerythritol (PER) as FR for PP have been studied (fig.5). Unexpectedly, the NPM Cu become very efficient synergist for APP+PER in PP fire retarded. In this case, the performance of the NPM Cu depends on the content in the formulations. For example, very sharp maximum is observed on the dependence of oxygen index (OI) on concentration of the nanometal at 0.05% wt. of Cu in PP+APP/PER, the OI increases from 26 to 32.

The effect of NPM Cu on the thermal degradation of PP and PP+APP/PER have been studied (fig. 6). It is established that NPM Cu affects the thermal degradation of PP. The thermal degradation of original PP proceeds in one stage, whereas the decomposition of PP in the presence of NPM Cu does in three. The addition of NPM Cu exerts great effect on thermal degradation mechanism of PP. In the presence of NPM Cu, the initial temperature of decomposition of PP decreases by 60^{0}C (260^{0}Ñ for original PP and 200^{0}Ñ for PP+Cu). Also, in the presence of Cu there is 30 % yield of char formation 700 ^{0}Ñ temperature. Laser pyrolysis conjugated with the mass-spectrometry analysis was used to study the products of

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mass-spectrometry analysis was used to study the products of degradation of PP+Cu (Table 2).

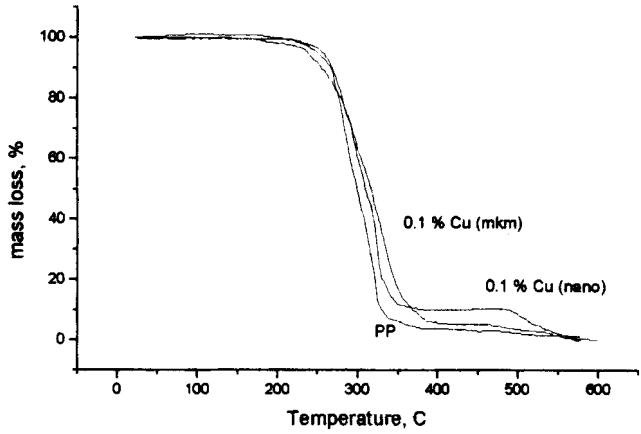

Fig.6 The effect of the particle size of NPM Cu on the thermal degradation of PP.

The presence of NPM Cu results in formation of aromatics and acetylenes. In contrast, decomposition of neat PP and PP containing Cu with particle size larger than 200 micron (mkm) does not lead to these products. In addition, unsaturated hydrocarbons are produced in the presence of NPM Cu. It is likely that NPM Cu catalyses dehydrogenation of the polymer, which leads to the cross-linking and aromatization during thermal decomposition of PP.

According to IR-spectra of solid residues, NPM Cu significantly accelerate the thermooxidative degradation of PP. The addition of NPM to PP+APP slowly retards the process of oxidation of PP which is most likely due to interaction between hydroxyl groups of oxidized PP and APP. It is difficult to discuss about the influence of NPM Ñu on the solid residue of PP+APP/PER during degradation since the IR-spectra of PP+APP/PER and PP+APP/PER+Cu are the same. However we can suggest that NPM Cu accelerates the interaction (esterification reaction) between APP and PER.

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Table 2. The mass-spectrometry analysis data of the laser pyrolysis of PP+Cu (0.1 %).

Hydrocarbons	Size particle			
	-	> 200 mkm	10-100 mkm	3-50 nm
Ñ	97,4	97,2	88	91,0
Àlknes	0,1	0,1	10-100	0,5
Àlkenes	0,1	0,1	88,0	0,6
Àcetylenes	-	-	0,1	0,6
Àromatics	-	-	0,1	0,7
Oxygen-containing	-	-	0,1	0,5

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