Grafted polypropylene with bonded chlorine, bromine, and phosphorus compounds

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*Dedicated to Professor Ing. J. Beniska, DrSc., in honour of his 60th birthday*

Compounds containing chlorine, bromine or phosphorus were bonded on surface-grafted polypropylene with 2,3-epoxypropyl methacrylate by means of epoxy groups. The polymer with bonded monophenylphosphoric acid containing 0.4—1.2 mass % phosphorus in the solid phase had properties of a self-extinguishing material.

It was proved by thermal analysis that some fixed compounds retard effectively exothermal reactions in the material, when they are heated in air. The increased stability in the temperature range 200—300 °C could be also significant for the polymer protection during its thermal processing.

Соединения, содержащие хлор, бром или фосфор, были навязаны через эпокси-группы на поверхность привитого полипропилена с 2,3--эпоксипропилметакрилатом. Полимер с навязанной монофенилфосфорной кислотой, содержащий 0,4—1,2 % по массе фосфора, имеет в твердом состоянии свойства самотушащего вещества.

С помощью термического анализа было доказано, что некоторые связанные вещества эффективно замедляют экзотермические реакции в материале при нагревании на воздухе. Повышенная устойчивость в промежутке температур 200—300 °C может также иметь значение для защиты полимера при его термической обработке.

It is possible to bond compounds containing a labile hydrogen (HX) on polypropylene (PP) grafted with 2,3-epoxypropyl methacrylate according to Scheme 1 [1, 2], where X can have a special effect on the polymer. Such fixed
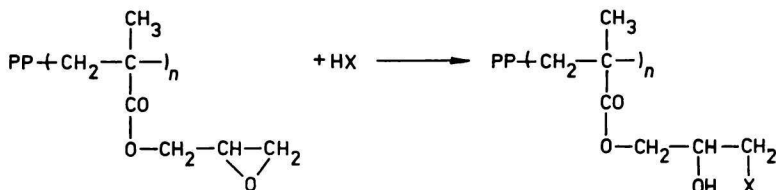
Scheme 1

compound does not escape from the polymer during the thermal processing and application.

In this work compounds containing chlorine, bromine, and phosphorus were bonded on grafted PP. The heat resistance of the materials obtained was evaluated by thermal analysis.

Experimental

Chemicals

Isotactic, unstabilized, powdered polypropylene, Tatren HPD, with a melting flow index $2.2\,g\,10^{-1}\,min^{-1}$ and bulk mass $0.4\,kg\,dm^{-3}$ was produced in Slovnaft, n.e., Bratislava. This polypropylene was grafted with 2,3-epoxypropyl methacrylate (EPM) in aqueous emulsion [3]. The grafted polypropylene (PP—EPM) contained 1.5 mass % epoxy oxygen.

The fixed compounds, such as 3,5,3′,5′-tetrabromo-2,2-dihydroxydiphenyl (TBP), 2,6,2′,6′-tetrabromodian (TBD), and metaphosphoric acid (MPA) were of anal. grade; hydrobromic acid (BAA) and dichloroacetic acid (CAA) were purified by rectification, monophenylphosphoric acid (PPA) was purified by recrystallization from acetone.

Triethylamine (TEA), purified by rectification, was used as catalyzer for the fixation of compounds on the epoxide group of PP—EPM. Dioxan and heptane, anal. grade, were solvents for the fixed compounds and catalyzer. Purification of PP—EPM with the fixed compound from the unreacted components was carried out with methanol and acetone of anal. grade. Fixation of the compounds was provided under nitrogen, which was purified on a packing of 55 % MnO_2, 40 % MgO, and 5 % Cr_2O_3.

Procedures and equipment

Bonding of compounds containing an acidic hydrogen on the epoxy groups of PP—EPM was carried out in sealed glass ampoules in nitrogen atmosphere. The system, which was the whole time heterogeneous, contained 1 g PP—EPM and $5\,cm^3$ of the solvent mixture of $4.5\,cm^3$ of n-heptane with $0.5\,cm^3$ of dioxan, in which 200 mol % of the fixed compound with respect to the epoxide of PP—EPM was dissolved. In most cases the catalyzer TEA was present in the ratio $n(\text{TEA})/n(\text{epoxide}) = 10$ %. The reaction proceeded in a bath at 95 °C. After 3 h the solid phase with the bonded compound was poured into $200\,cm^3$ of methanol and after 24 h it was filtered off on a sintered glass filter S_2, where it was washed with methanol, water, and acetone. It was dried at room temperature to the constant mass. The content of the fixed compound in the solid phase was calculated in mass % from the mass increase of the sample after the reaction and from the elemental analysis of the characteristic element.

The thermal analysis of the samples was carried out under oxidation (air) as well as under inert atmosphere (nitrogen) by means of the Thermoanalyzer Mettler. 9 mg material was weighed, the heating rate was $10\,°C\,min^{-1}$ and the flow rate of the carrier gas was $7\,dm^3\,h^{-1}$.

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The oxygen index of the samples (LOI, vol. % of O_2) was determined in the range of the standard deviation ± 0.1 LOI by a modified procedure according to the Czechoslovak standard ČSN 640756 for powdered materials using the Stanton—Redcrofts device, determining the oxygen concentration by a paramagnetic analyzer. The 0.5—1.0 g sample in powdered form was ignited with a glowing spiral under the atmosphere of a mixture of O_2 and N_2 at a gas flow rate 15 dm³ min⁻¹ As LOI was estimated the oxygen concentration at which the sample burns for 180 s or at which the sample is burned through the surface into the depth of 5 mm.

Results and discussion

In Table 1 the composition of the polymers obtained with bonded compounds containing chlorine, bromine, and phosphorus, eventually their mixtures and simultaneously also the determined LOI values, which provide in-

Table 1

Composition of PP—EPM with bonded compounds and their influence on the LOI value of the material

Fixed compound		Content of the element $w_i/\%$			LOI $\varphi(O_2)/\%$
Type	$w_i/\%$	Br	Cl	P	
BAA	10.3	5.9			20.8
TBP	14.0	8.9			20.8
TBD	16.1	9.4			19.3
CAA	12.4		6.8		19.2
MPA	5.4			2.1	18.8
PPA	6.1			1.2	23.4
TBP[a]	7.0	4.5			
PPA	3.0			0.6	22.4
BAA[a]	3.4	2.0			
CAA	4.1		2.3		
PPA	2.0			0.4	21.2
TBP[a]	7.0	4.5			
MPA	2.7			1.1	20.5
TBP[b]	16.0	10.2			
MPA	3.4			1.3	20.9
—[c]	—				18.8

a) Mechanical mixture with separately fixed compounds; *b)* both compounds were fixed subsequently on the same PP—EPM; *c)* reference PP—(OH)₂ sample.

formation about the combustibility of the material is shown. The contribution of the fixed compound to the retardation of the combustion was evaluated with respect to the reference sample PP—(OH)$_2$. The latter is a PP—EPM, in which the epoxy groups were hydrolyzed [2].

From Table 1 is evident the extraordinary position of the fixed PPA with respect to the influence on the decrease of combustibility of PP—EPM in comparison with samples containing halogen. The phosphorus concentration is yet rather low; and even if it is decreased to 1/3 the LOI value reaches a value, which is over the self-extinction value of the material (the material does not burn in test conditions in air).

PP—EPM with bonded PPA was thermally analyzed. For comparison also some thermoanalytical characteristics of the mixture of PP—(OH)$_2$ and PPA with equal amounts of the components, and of PP—(OH)$_2$ and PPA alone were measured (Figs. 1 and 2, Table 2).
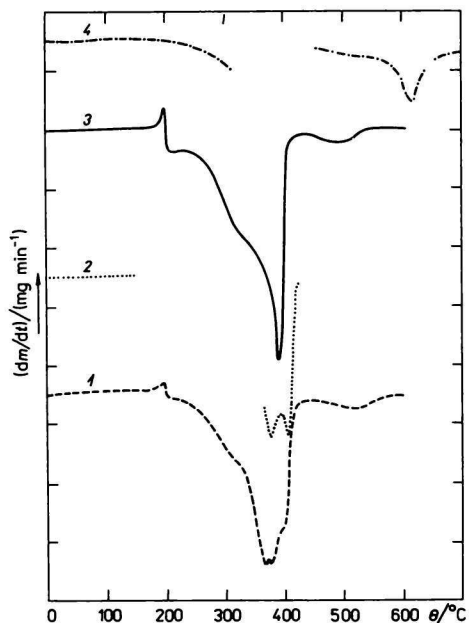

Fig. 1. DTG record of PP—EPM with bonded PPA (PP—EPM—PPA), PP—(OH)$_2$ + PPA mixture, and PPA and PP—(OH)$_2$ alone.
1. PP—EPM—PPA; *2.* PP—(OH)$_2$ + PPA; *3.* PP—(OH)$_2$; *4.* PPA.
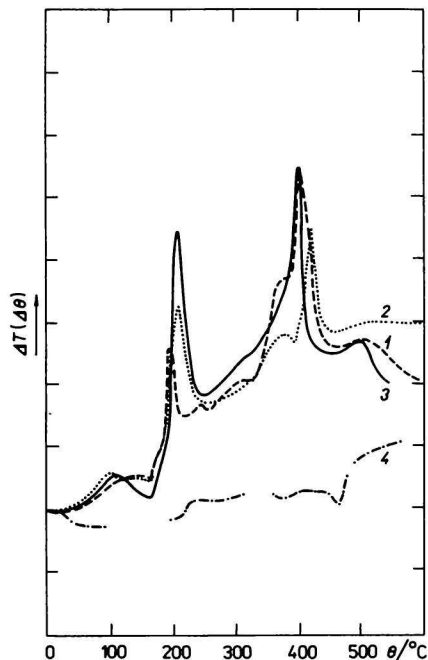
Fig. 2. DTA record of PP—EPM with bonded PPA (PP—EPM—PPA), PP—(OH)$_2$ + PPA mixture, and PP—(OH)$_2$ alone in air and nitrogen atmosphere (PP—(OH)$_2$, N$_2$).
1. PP—EPM—PPA; *2.* PP—(OH)$_2$ + PPA; *3.* PP—(OH)$_2$; *4.* PP—(OH)$_2$, N$_2$.

Table 2

Thermoanalytical characteristics of PP—EPM with fixed PPA (PP—EPM—PPA),
PP—(OH)$_2$ + PPA mixture, and PPA and PP—(OH)$_2$ alone[a]

Analyzed material	Decomposition stage	θ_{init} °C	$\Delta\theta$ °C	Δm_r %	θ_{max} °C	$(dm/dt)_{max}$ mg min^{-1}	R(300 °C)/%	R(600 °C)/%
PP—EPM—PPA	I	243	243—325	20.9	325	0.60	85.9	
	II		325—443	63.7	368	1.45		
	III		443—600	10.2	512	0.10		2.5
PP—(OH)$_2$ + PPA	I	253	253—330	15.8	330	0.60	86.5	
	II		330—450	65.4	383	1.35		
	III		450—600	8.2	526	0.10		6.0
PP—(OH)$_2$	I	247	247—320	22.3	320	0.87	82.5	
	II		320—425	64.0	395	1.95		
	III		425—535	5.7	500	0.10		2.5
PPA	I	230	230—427	42.7	364	0.73	93.3	
	II		427—578	14.0	578	0.17		
	III		578—682	22.3	626	0.50		38.8
	IV		682—900	13.8	745	0.15		

a) θ_{init} — temperature, at which the active mass decrease of the sample begins, θ_{max} — temperature, at which the decomposition of the sample takes place at maximum rate, m — mass of the sample, R — undecomposed residue of the sample at the given temperature.

The active thermal decomposition of the polymer carrier PP—(OH)$_2$ takes place in more steps. The first changes of the polymer carrier have a thermooxidation character (Fig. 1 (DTG)) and are accompanied with a low mass increase (1.3 %). The changes have an exothermal character (Fig. 2). An endothermal minimum is observed at the melting temperature of the polymer carrier. The melted polymer carrier is oxidized faster, when the temperature is further increased, but at temperatures over 200 °C also decomposition reactions take place, which can be seen from the fast mass decrease (Fig. 2). Further forming of volatile products takes place under the air atmosphere in the temperature range 247—425 °C, and under the inert atmosphere (nitrogen) in the range 247—500 °C. It is possible to divide this area into two phases with different temperature ranges 247—320 °C and 320—425 °C (for the air atmosphere) and 247—370 °C and 370—500 °C (for the inert atmosphere). Further oxidation of the residue enriched with carbon proceeds in the temperature range 425—535 °C.

The calculated apparent activation energy of PP—(OH)$_2$ gasifying [4] under the air atmosphere is for the temperature range 300—400 °C 74 kJ mol^{-1} and under nitrogen 244 kJ mol^{-1}. The values are in good agreement with the published ones for polypropylene [5].

The fixed PPA or its mixture with PP—(OH)$_2$ markedly decrease the exothermal effects during the thermal decomposition of the material under air. This is significant in the area of about 200 °C, where due to this effect a decrease of the absorbed oxygen is observed as well as a decrease of the exothermic peak height and a shifting of the latter toward the lower temperatures. With regard to this the fixed PPA form is more efficient. The retardation of the initial thermooxidation phase is important for the processing of polymers at elevated temperatures. The presence of both forms of PPA does yet not markedly influence the apparent activation energy of the thermolysis in the temperature range 240—450 °C.

Table 3

Some thermoanalytical characteristics of PP—EPM with bonded halogen and calculated apparent activation energies of thermolysis (E)[a]

Fixed compound	θ_{init}/°C	θ_{max}/°C	$\Delta\theta$/°C	E/(kJ mol^{-1})
CAA	220	420	300—350	39
			370—430	92
BAA	246	420	320—360	49
			380—430	115

a) The same symbols as in Table 2.

On the contrary the material with bonded halogen, such as CAA or BAA, is characterized by the thermal analysis by two linear sections in the TG record. The first one corresponds to the decomposition of the bonded halogen compound and the second one to the decomposition of the polymer. Each of both sections is characterized with a different activation energy (Table 3).

The exothermal effect is markedly depressed in the area at 200 °C by the influence of bonded CAA or BAA; the characteristic peak of it appears not before 420 °C and 450 °C, respectively. BAA in fixed form is characterized by a greater heat stability than CAA, mainly in the initial stage of the thermolysis. This is probably dependent, besides of other factors, also upon its greater ability to retard burning of polymers. However, in comparison with the effect of PPA these materials are less active, which is caused in great deal by the fact that they are gasified already before the main decomposition of the basic polymer.

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