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THERMOANALYTICAL INVESTIGATION OF GRAFTED POLYPROPYLENE WITH FIXED FLAME RETARDANT COMPOUNDS

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ABSTRACT

The samples of isotactic modified polypropylene with bonded flame retardants have been analyzed by the DTA, TG and DTG method. The retardants applied contained halogens or phosphorus. Primarily the material with a 1.3 % phosphorus content had an elevated resistance to oxidation in the range of temperatures 200-300 °C and, at the same time, the highest oxygen number. The materials bonded from polymer do not volatilize after its thermal treatment.

INTRODUCTION

A large variety of polymer additives /stabilizing and antistatic agents, flame retardants, cross-linking agents, etc./ considerably modify the properties of particular polymeric materials, thus extending the scope of their utilization. The majority of additives are low-molecular volatile materials that can leak out from the polymer material during its treatment or utilization. Since the above materials are very often harmful, they also negatively affect the enviroment. One of the possibilities to increase the additives fixation is their chemical bonding to a basic polymer. The best elaborated mode of stabilizers fixation is that used for polymers[1]; other additives are given less attention. Upon using grafted polypropylene as a universal carrier of reactive groups the polymer can be cross-linked, and the antistatic agent or flame retardant can be bonded. The latter additive is, from the fixation point of view, higly topical mainly for the fact that here the halogen containing toxic materials are applied [2-4]. An effort has been made to fix to the polymer also the materials of the combined effect [5]. In this work we have considered the possibilities of selected, halogen or phosphorus containing materials being bound to polypropylene, and to retardate the polymer burning on the basis of its TA results and of the measured oxygen number /LOI/ as well.

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CHEMICALS AND MEASURING METHODS

Isotactic powdered polypropylene /PP/ was grafted by 2,3-epoxypropylmethacrylate /EPM/ in water emulsion [6]. PP-EPM contained 1.5 % of epoxy oxygen. Substances such as 3,5,3,5-tetrabromo-2,2-dihydroxydiphenyl /TBDP/, bromoacetic acid /BRAA/, dichloroacetic acid /DCAA/, and monophenylphosphoric acid /MPPA/ were pure. Triethylamine /TEA/ was analytically pure.

The chemical fixation of compounds with the presupposed retardation effect of combustion upon PP-EPM was accomplished in the oxygen atmosphere at 95 °C [1]. The retardant /200 molar per cent with regard to epoxid/ and the TEA activator /10 molar per cent/ that were dissolved in 5 ml of the n-heptane-dioxane mixture at the vol.ratio of 9:1 were added to 1 g of EPM polypropylene. After 3 hours of reaction a solid polymer phase was trapped on sintered glass where it was purified and dried. Table 1 indicates the contents of bonded elements in the samples prepared.

The oxygen number of the samples /LOI/ was established by the Stanton Redcroft /England/ equipment. In this case the Czechoslovak standard No 640756 modified to powdered material was applied.

TA of the samples was carried out on the Thermoanalyzer equipment /Mettler firm/ under these conditions: sample weight ca 90 mg, heating rate of 10 °/min, a narrow platinum crucible, reference sample, the overannealed Al_2O_3, DTA sensitivity of 200 μV, PtRh thermocouples /10%-Pt/, DTG sensitivity of 5 mg/min, dynamic air atmosphere, rate of air flow of 7 dm^3/hr.

RESULTS AND DISCUSSION

The characteristic data of TA polypropylene with bonded flame retardant, shown in Table 1, point out to a relatively favourable thermal stability of materials which undergo 300 °C temperature in the fibre preparation. This is evident from the course of DTG and DTA recordings for the systems 3, 4 and the system 5 shown in Figs. 1 and 2. The DTG recording /Fig.1/ illustrates that the presence of flame retardant is responsible for the essential decrease in the highest rate of oxidative polymer degradation compared to PP. In the temperature region of 22 - 300 °C used in treatment of PP one may observe some exothermic effects /Fig.2/ restricted by the presence of retardants, particularly with the application of bonded MPPA; an exotherm is transmitted approximately as high as *the temperature of 450 °C. From the DTA results an inhibition period of thermooxidation is possible to be determined.[7]*

The correlation of DTA results with LOI of the samples /Table 1/ indicates good agreement mainly for the system 4 with bonded MPPA; other materials cause a flammability decrease of PP as far as to the boundary of self-extinction. From this aspect there is no remarkable difference between the bromine materials /systems 1 and 3/ and the chlorinated ones/2/. The bonded MFF is efficient also with the threefold lower concentration /LOI = 21,2/.

The additional types of polymeric synthesis are dependent on the accessibility of suitable fixation materials.

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Table 1 TA of the PP samples with bonded flame retardants and their oxygen numbers /LOI/

No	Fixation material	Element, %			LOI	DTG		DTA		$R_{600\,°C}$
		Br	Cl	P		$°C_{max}$	mg/min	$°C^{exo}_{max}$	μV	%
1	BRAA	5,2			20,8	418	1,8	430	57	2,0
2	DCAA		6,3		19,2	420	1,6	443	53	1,5
3	TBDP	6,2			20,8	389	1,1	473	64	0,5
4	MPPA			1,3	23,4	368	1,5	406	60	2,0
5	-				18,8	416	2,0	425	56	2,5

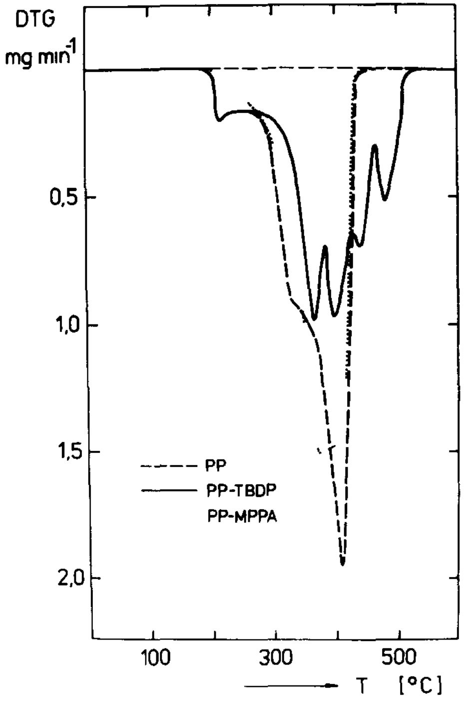

Fig. I DTG curves of pure PP and of PP with bonded flame retardants

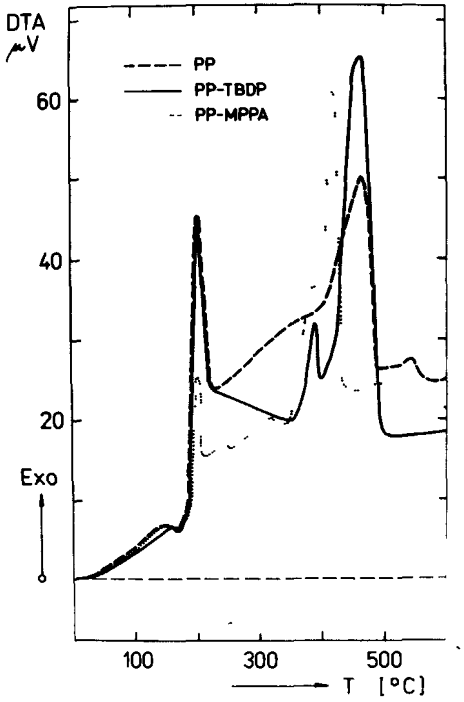

Fig. 2 DTA curves of pure PP and of PP with bonded flame retardants