Journal of Thermal Analysis and Calorimetry, Vol. 62 (2000) 485–490

STUDY OF THERMODESTRUCTION PROCESSES IN POLYPROPYLENE/EXFOLIATED GRAPHITE COMPOSITES

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Abstract

In the present paper the effect of the thermoexfoliated graphite (EG) content (0–0.310 parts by volume), constituent mixing conditions (a paddle mixer or a disk-and-screw extruder), annealing and aging on thermodestruction processes of polypropylene (PP)/exfoliated graphite composite materials (CM) by means differential thermal analysis and the thermogravimetric method have been investigated. The studies have shown that thermodestruction processes in CM based on PP and EG ran in air for expense of PP thermodestruction. The characteristics of thermodestruction in CM essentially depend on a regime of making and concentration of components. It is established that processes leading to the formation of less perfect crystalline structures or causing amorphization of PP (including formation of continuous space structures from EG particles, cluster traps) advances thermodestruction. The increase in crystallinity extent of PP favors to the decrease in thermodestruction processes.

Keywords: composites, polypropylene, thermodestruction, thermoexfoliated graphite

Introduction

Thermoexfoliated graphite (EG) is one of the prospective components to produce efficient composition materials (CM) and products possessing a corrosion resistance, conductivity, a valuable complex of thermophysical and elastic-plastic properties [1, 2]. Materials based on EG are used to manufacture electrodes, resistive elements of heaters, wear-resisting parts, vibroresistant gaskets and for other purposes [1–4]. A number of studies [3–8] has been carried out for detailed study of electrophysical, mechanical and other properties of CM in systems polyethylene (PE)–EG, polypropylene (PP)–EG, polyamide–EG while changing a volume fraction of graphite (θ) from 0 to 1. However, data on processes of thermodestruction in polymer–EG composition materials are practically absent in literature.

The purpose of the present paper is to investigate an influence of an EG content and preparative conditions of CM on thermodestruction processes of polypropylene – EG composition materials.

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Results and discussion

To interpret the results obtained we use a proposed concept of formation of structure and properties of polymeric composition systems (PCS) which is based on a cluster approach, percolation processes in PCS, ideas of formation of fractal structures [8].

To produce polymeric blends and CM a low pressure PP of type 21030-16 (GOST 26996-86) and EG of type GAKV-2 (particle size 0.1–3.0 mm, specific surface area 56 m^2 g^{-1}) were used. PP and EG were melted in a paddle mixer or in disk-and-screw extruder (EKG-45) by a traditional technology [7]. An EG content was varied from 0 to 0.31 of a volume fraction (50 mass%). Samples of several types (variants) were prepared for a differential thermal analysis (DTA) and thermogravimetry, namely:

1. Mixtures of PP and EG prepared in melt using a paddle mixer at a temperature of 190±2°C.

2. CM prepared from mixtures of 1 variant by a method of hot pressing at a temperature of 170±2°C followed by cooling at a rate of 20°C min^{-1}. The samples were prepared without annealing.

3. CM prepared by variant 2 and then annealed for 5 h at a temperature of 114±2°C and cooled at a rate of 5°C min^{-1}.

4. CM produced by a method of hot pressing (similarly as in variant 2) from composition mixtures produced by mixing in a disk-and-screw extruder [7] in experimental-production conditions. Temperature in the third zone of an extruder was 184±2°C.

5. EG produced by cold pressing under 15 MPa. Plates of CM for DTA and EG were milled.

Differential thermal analysis and thermogravimetric studies were conducted by using a derivatograph of Q-1500 M type. The heating rate was 5°C min^{-1}, the weighed portion was 0.6 g. Curves of TG, DTG and DTA were automatically recorded. As criteria of an estimate of thermodestruction processes in CM, next parameters were used: T_1 (a temperature of loss of 10% mass), T_2 (a temperature of a maximum rate of mass loss), T_3 (a temperature of minimum of a general endothermic process of thermodestruction). These parameters were determined from the respective curves of TG, DTG and DTA. Previously in [7] we have determined the above-mentioned CM samples temperature of melting (T_m), melting effects, a degree of crystallinity (χ, %) of PP from the DSC curves.

DTA curves of unfilled PP and CM with a different EG content are given in Fig. 1. Characteristics of processes of CM thermodestruction are presented in Table 1. It was established that an unfilled PP had such values of thermodestruction characteristics: T_1=370°C, T_2=T_3=432°C.

For EG (no polymer, variant 5), a temperature of onset of mass loss is 470–480°C, and T_1=660°C. Therefore, thermodestruction processes in CM based on PP and EG run in air at the account of PP thermodestruction. At present, there are no clear understanding of mechanisms of PP oxidation and on the correspondence of

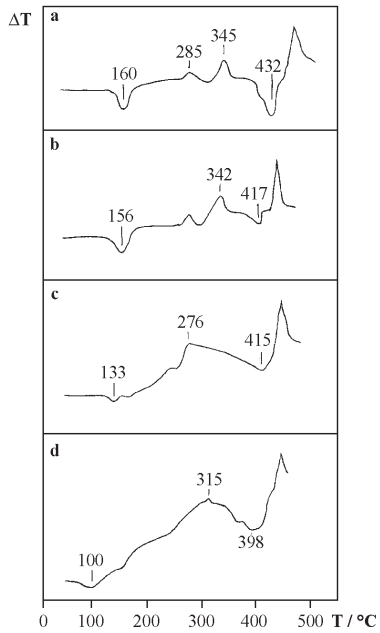

Fig. 1 DTA curves of unfilled PP and CM with various EG volume fraction (θ): unfilled PP θ=0 (1); θ=0.023, 0.074 and 0.310 (2–4 respectively)

peaks of oxidation to definite processes of thermodestruction. However, a general endothermic peak (T_3) is associated usually with processes of PP depolymerization [9].

It was of interest to clarify the effect of EG content on processes of thermodestruction of CM produced by mixing components in a paddle mixer followed by pressing (variant 2). As seen from Table 1, introduction of even low EG amounts into composition of CM (0.0045 volume fraction EG) causes a decrease in T_1 by 9°C. A further increase in EG content in CM advances an increase in intensity of thermodestruction processes in CM and leads to a shift of T_1, T_2, T_3 towards lower temperatures. Doing so, the shape of DTA curves is also changed (Fig. 1). We associate the observed effects with the change of CM structure when increasing an EG content.

Previously [6] it was established based on studies of the structure of samples of polypropylene/EG CM using microscopy and electrophysical methods, that a system PP–EG (a range of studies from 0 to 1 volume fraction of EG) has 2 thresholds of percolation (q_c and q'_c). Here, when the concentration of EG $q=q_c=0.02$, a continuous fractal cluster of EG particles is formed, at $q=q'_c=0.05$ a continuous cluster of PP particles disappears. Thus, a CM structure in the range of EG content $0<q<0.02$ represents a PP matrix including isolated clusters of EG particles. In the range of $0.02<q<0.05$ ($q_c<q<q'_c$) a continuous cluster of PP and EG exist simultaneously. In the range of $0.05<q<1$, macrostructure of CM represents a branched continuous fractal cluster of EG particles (a continuous phase), and clusters of PP are isolated inclusions [6, 7].

Table 1 Characteristics of thermodestruction processes of unfilled PP and PP/EG composite materials

EG content, volume fraction	Variant	T_1/	T_2/	T_3/	Equipment for the mixing of components	The presence of annealing
		°C				
0	1	370	432	432	without mixing	without annealing
0.0045	2	361	432	432	a paddle mixer	without annealing
0.0230	2	357	417	417	a paddle mixer	without annealing
0.0354	2	341	420	405	a paddle mixer	without annealing
0.0354	3	304	405	405	a paddle mixer	after annealing
0.0480	2	300	400	420	a paddle mixer	without annealing
0.0480	4	350	438	440	a disk-and-screw extruder	without annealing
0.0740	2	277	411	415	a paddle mixer	without annealing
0.1620	2	277	400	400	a paddle mixer	without annealing
0.3120	2	260	398	398	a paddle mixer	without annealing

A formation of a continuous branched multifractal cluster of EG at q=0.075 leads to a considerable decrease of T_1 (by 93°C), T_2 (by 21°C), T_3 (by 17°C). A further increase in EG content in CM does not cause such considerable changes in thermodestruction characteristics (Table 1). One of the reasons of the above-mentioned changes in thermodestruction processes may be the formation of multiple ways in supply of oxygen in PP areas at formation of a continuous branched cluster of EG. However, a main factor of intensification of thermodestruction processes is a formation of imperfect crystalline PP structures, and a decrease of its degree of crystallinity in CM due to a formation of continuous structures of particles of EG and cluster traps. For example, at q=0.035 of a volume fraction EG a fall of a melting temperature by 16°C and a degree of crystallinity by 10% as compared to unfilled PP (T_m=161°C, χ=40%) takes place. At concentration of q=0.074 in CM a temperature of melting decreases by 28°C and a peak of melting is not expressed clearly. At q=0.31 in CM a peak of melting is absent, that indicates amorphization of PP in CM [7].

The thermodestruction processes in CM depend considerably on technological parameters of CM processing. These especially strong processes are influenced by a type of equipment used on mixing PP and EG.

It is shown that for the same composition (volume fraction of EG is 0.047) and the same pressing conditions CM samples produced by mixing in disk-and-screw extruder, have higher values of T_1 and T_2 than samples from mixtures made in a paddle mixer. In addition, values of T_2 of the latter by 6–8°C exceed the corresponding temperatures of unfilled PP.

Previously [6, 7] it has been shown that the use of a paddle mixer provides relatively mild mixing conditions at low shift stresses that promotes a conservation of structure forming properties of EG in melt and formation of chain structures of EG in CM. Significant shift stresses under mixing in disk-and-screw extruder advance a destruction of continuous chain structures of EG and formation of ordered spherolytic structures of PP [7]. Thus, for the CM sample containing 0.047 volume fraction of EG (variant 4, the use of extruder while mixing components) T_m=160°C, a degree of crystallinity is 35.5%. For the CM sample of the same composition prepared by the regime 2, T_m=145°C, χ=31.1% that is considerably lower than for a sample in variant 4.

Thus, data of processes of thermodestruction in the studied CM correlate well with the results of formation of EG and PP structures. EG clusters are a steric hindrance for a growth of permolecular formations of PP. Near the EG surface, mobility of polymer chains is lowered, their mechanical wedging in pores and defects of EG [7] is also possible. The above-mentioned factors promote amorphization of PP in CM. The results obtained are consistent to data of works [9] which report that processes of oxidation and thermodestruction in an amorphous PP run more intensely than in a crystalline PP.

For the formation of more equilibrium and thermodynamically stable structures, samples of an unfilled PP and CM were exposed to annealing by the regime of variant 3. It was found that a degree of influence of annealing on thermodestruction processes depends on an EG concentration in CM. In addition, values of thermodestruction are in interrelation with a degree of crystallinity of PP in the CM sample. For instance, at content of q=0.053 of a volume fraction of EG, values of T_1 and T_2 lowered as compared to an unannealed sample. In this way, a degree of crystallinity of PP in the sample was also lowered from 33.9% (for an unannealed sample) to 30.3% (for annealed one).

Besides the above-mentioned tests, an effect of a natural aging was studied on storage of samples at temperatures of 20–23°C for 1 year. It was established that values of T_1, T_2, T_3 increase in the case when recrystallization of PP occurs during aging and its degree of crystallinity in CM increases.

Conclusions

It was shown that the characteristics of CM thermodestruction depend strongly on an EG concentration, technological conditions of making CM, conditions of annealing and aging. It was established that in a majority of cases a decrease in T_1, T_2, T_3 values correlate with lowering a degree of crystallinity of PP in CM and this is due to the formation of continuous prolonged clusters of EG and cluster traps of its particles.

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