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THERMAL ANALYSIS OF THE POLYMERIZATION PROCESS ON THE SURFACE OF INORGANIC FILLERS

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Abstract

The thermal polymerization of pentabromobenzyl (mono)acrylate (PBB-MA) on the surface of the inorganic fillers $Mg(OH)_2$ and $CaCO_3$ was studied. FTIR spectroscopy and extraction of the polymer in bromobenzene show that polypentabromobenzyl acrylate (PBB-PA) was mostly grafted on the surface of $Mg(OH)_2$. Thermal analysis (TG, DSC, isothermal DSC (IDSC)) demonstrated an increase in polymerization starting temperature, and differences in polymerization enthalpy and apparent activation energy when an inorganic filler is added. These differences depend on the chemical composition of the filler used.

Keywords: DSC, FTIR, grafting, IDSC, kinetic parameters, polymerization, TG, thermodynamic parameters

Introduction

Inorganic fillers are widely used for plastics production. They improve some properties of plastics and reduce their prices [1–3]. In flame-retarded plastics some inorganic fillers are also used for other purposes, for example, magnesium hydroxide is used as a smoke suppressant [4].

However, the main problem is that inorganic fillers can also decrease the impact energy because of poor adhesion between the filler and the plastic matrix [5]. Normally the surface of inorganic fillers is specially treated with a coupling agent to improve the performance of fillers is specially treated with a coupling agent to improve the performance of fillers in plastics, but sometimes toxic materials such as silanes are used [6–11].

For flame-retarded plastics we have developed another method to improve matrix-filler adhesion. This method consists in the thermal polymerization of flame-retardant monomers on the surface of inorganic fillers followed by the application of the polymerizate to polymer matrix. Such approach provides a

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possibility to improve the thermal and mechanical properties of flame-retarded plastics [12].

Bromine-containing monomers are widely used flame-retardants capable of being polymerized either in a plastic matrix or without plastic. One of these monomers is pentabromobenzyl (mono)acrylate (PBB-MA) ($C_{10}H_5Br_5O_2$). The product of PBB-MA polymerization is pentabromobenzyl (poly)acrylate (PBB-PA) which acts in the following way: C_2H_5Br and $H^{\bullet}$ are formed in the first stage of polymer flaming as the result of thermal degradation of the polymer and PBB-PA. The following reaction occur:

$$C_2H_5Br+H^{\bullet} \rightarrow C_2H_6+Br^{\bullet}$$

$$Br^{\bullet}+RH \rightarrow HBr+R^{\bullet}$$

In this manner, the highly reactive chain-propagating species, $H^{\bullet}$, are replaced by the relatively nonreactive $Br^{\bullet}$ radical, which inhibits flame spread [13].

The application of thermal analysis to the study of polymerization is well known [14–15], but the influence of inorganic fillers on the polymerization process has not been studied in depth. One of the important questions is whether the polymer is grafted on the surface of the filler or is adsorbed by physical adsorption. The answer to this question may be found by means of FTIR method and by extraction of the homopolymer with a solvent [16]. These methods can provide information on the nature of the bonding between polymer and filler surface, but they cannot give us any information on the thermodynamic and kinetic features of the polymerization process, or on the influence of the fillers on the polymerization parameters. Thermal analysis (TG, DSC, IDSC) together with FTIR and extraction methods may provide this kind of information.

Experimental

In this study all the experiments were carried out with a crystalline monomer PBB-MA, and crystalline $Mg(OH)_2$ and $CaCO_3$ with an untreated surface and an average particle size of 1.5 μm. The crystallinity of $Mg(OH)_2$, $CaCO_3$ and PBB-MA was confirmed by X-ray spectroscopy. The inorganic fillers were admixed to PBB-MA, and the mixtures were compounded in a twin-screw extruder PLE-651 (Brabender) at 240°C with a screw rotation angle velocity of 377 rad min^{-1}. The filler content varied from 0% to 50%. The maximum filler concentration was 50% because it is the maximum filler content which can be extruded in this extruder with PBB-MA. Polymerizates with 25% of filler were tested. A mechanical mixture of the polymer and filler with the same filler content was used as a reference.

FTIR spectra were recorded with a Perkin Elmer 16 PC spectrometer, to evaluate the amount of residual monomer and to determine whether the polymer was grafted or only adsorbed on the surface of fillers. The specimens were prepared using KBr pellets. Additional data relating to the same question were obtained by extraction of the polymer with bromobenzene for 12 h at 152°C.

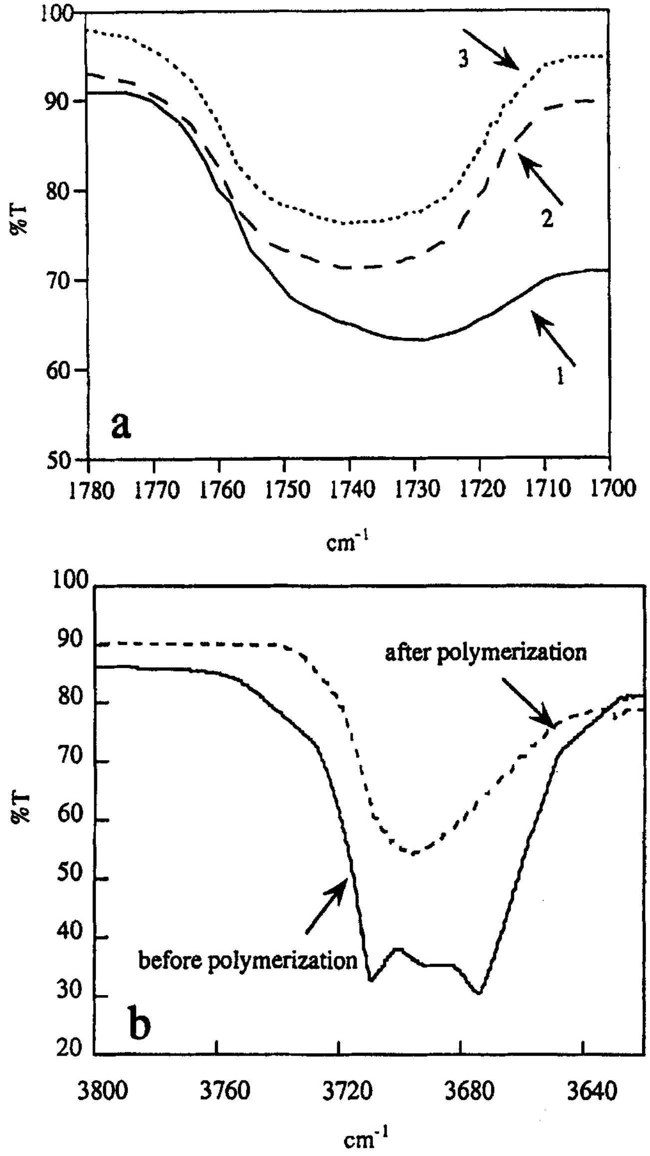

Fig. 1 FTIR spectra of PBB-PA mixed with fillers and polymerized on fillers: (a) the CO band (1-PBB-PA mixed with filler, 2-PBB-PA polymerized on $Mg(OH)_2$, 3-PBB-PA polymerized on $CaCO_3$), (b) the OH region

The thermal stability of PBB-PA was evaluated by TG in the temperature range 27–290°C and a heating rate of 10°C min^{-1}, using a Mettler TG50 instrument.

DSC curves were recorded with a Mettler DSC20 calorimeter. They were applied to determine the influence of inorganic fillers on such polymerization parameters as starting temperature and enthalpy. The heating rate was 10°C min^{-1} in all the DSC runs. From these curves information can be derived about the approximate starting temperature and about the enthalpy of polymerization. The approximate starting temperature can be read directly from the DSC curves as the temperature of observable deviation from the base line [17]. The polymerization enthalpies were calculated from the areas under the DSC curve, after correcting for the polymer and filler content, i.e. per weight of neat polymer. The kinetics of polymerization on the filler was studied by the isothermal DSC (IDSC) method. The test temperatures were selected in such a way as to permit evaluation of the kinetics of polymerization.

Results and discussion

The FTIR spectrum of pure PBB-PA is the same as the spectrum of the PBB-PA/filler physical blend. However, Fig. 1 demonstrates differences in the CO and OH regions between the spectra of PBB-PA mixed mechanically with $Mg(OH)_2$ and of PBB-PA polymerized on $Mg(OH)_2$. The following differences were observed between the mechanical mixture PBB-PA/$Mg(OH)_2$ and PBB-PA polymerized on $Mg(OH)_2$: the maximum of the C=O stretching band shifted from 1732 cm^{-1} for PBB-PA to 1738 cm^{-1} for PBB-PA polymerized on

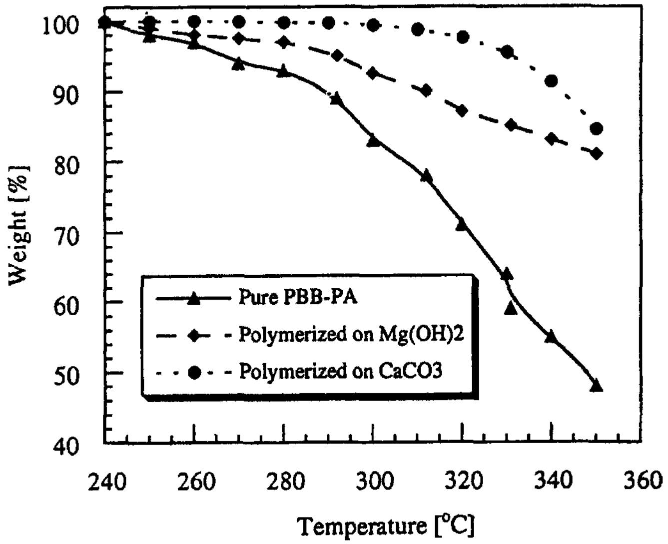

Fig. 2 TG curves of PBB-PA polymerized on fillers (50% PBB-PA/50% filler)

$Mg(OH)_2$ (Fig. 1a), and the shape of the O–H band for $Mg(OH)_2$ changed after polymerization (Fig. 1b). A displacement of the C=O FTIR band and the change of the O–H band of $Mg(OH)_2$ can be the result of chemical bonding between the polymer and the filler surface hydroxyls. A similar displacement of the C=O stretching band was observed when PBB-PA was polymerized on the surface of $CaCO_3$ (Fig. 1a). Thus, we assume that the thermal polymerization is accompanied by chemical bonding between PBB-PA and the fillers. 42% of the PBB-PA were extracted by bromobenzene from the PBB-PA/$Mg(OH)_2$ physical blend in 12 h at 152°C. Only 4% of PBB-PA homopolymer were extracted under the same conditions from the polymerizate with the same filler content. Similar results were obtained when $CaCO_3$ was used as a filler. The very small extent of extraction confirms the suggestion that the PBB-PA is mostly grafted on the surface of fillers.

The TG curves of the polymer mixed with filler are almost the same as the curve of a pure polymer. Figure 2 shows typical TG curves for PBB-PA polymerized on fillers. From these curves it is clear that the thermal stability of the polymerizate increases in the presence of a filler load. Fillers themselves do not lose mass at the temperatures of our tests, and we must take this fact into account when calculating the mass loss of the polymer. The mass loss of the polymer decreases to a minimum of about 20–30% with an increase of filler

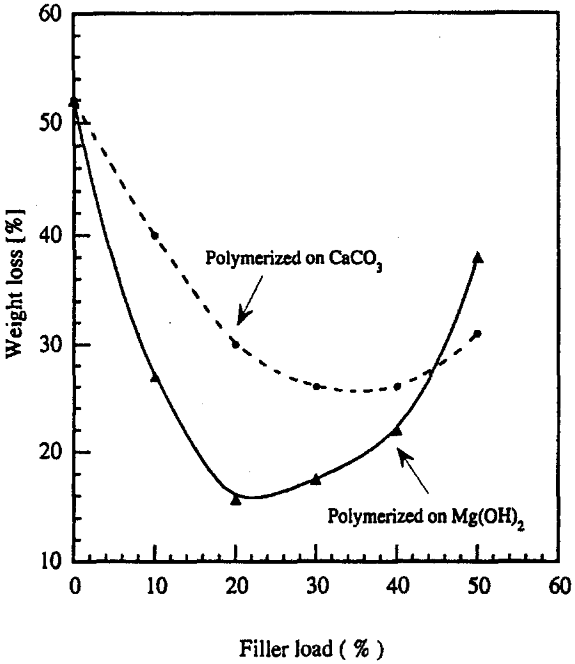

Fig. 3 Mass loss of PBB-PA polymerized on $CaCO_3$ and $Mg(OH)_2$ as a function of the filler load at 350°C

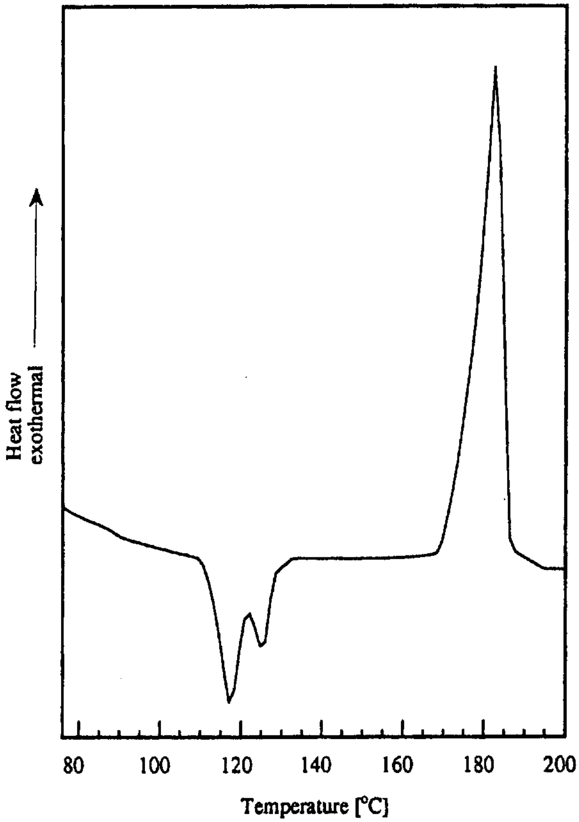

Fig. 4 An example of a DSC curve for PBB-MA polymerization on fillers

load (Fig. 3) up to 20 or 40% of $Mg(OH)_2$ or $CaCO_3$ respectively. Further increase of the filler load leads certainly to decreased polymer mass loss, but this mass loss is still lower than for the polymer without filler. An interesting fact is that the thermal stability of PBB-PA depends on the chemical nature of the filler: $Mg(OH)_2$ or $CaCO_3$. So, one can assume that this phenomenon is caused by the different chemical bonding between the polymer and the different filler.

Figure 4 picts a typical DSC curve for the PBB-MA polymerization. One can see the endothermic multiple melting peaks of the crystalline monomer and the exothermic polymerization peak. The multiple melting peaks of the monomer can explained by the separation of initial melting, monomer recrystal- lization and melting of the recrystallized monomer [8].

An increase of the polymerization starting temperature with an increase of inorganic filler load (Fig. 5) can be explained by the lower motion of the monomer molecules adsorbed on the surface of the filler or by the difference in heat capacities between filler and monomer. The polymerization starting temperature of PBB-MA depends on the chemical nature of the filler (Fig. 5). Taking

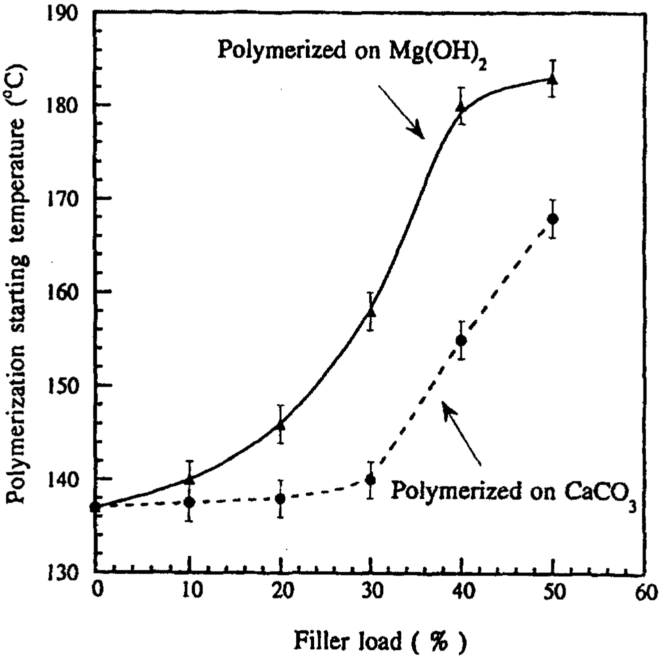

Fig. 5 Polymerization starting temperature as a function of the filler content

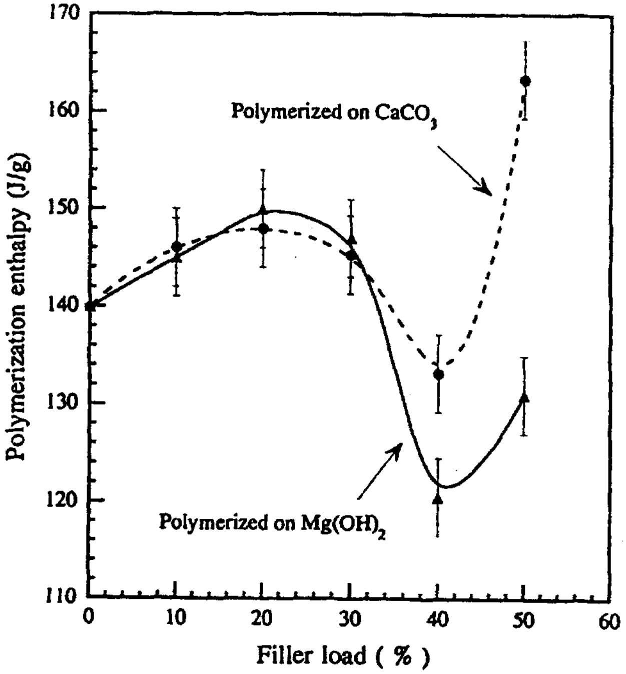

Fig. 6 Polymerization enthalpy as a function of the filler content

into account the fact that the starting temperature of polymerization characterizes the initiation of the polymerization chain, it may be supposed that the bonding between the polymer and the filler surface is the main reason for the increasing polymerization starting temperature.

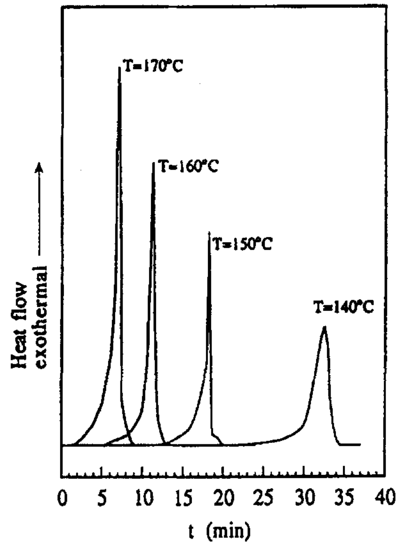

Fig. 7 An example of IDSC curves for PBB-MA polymerization on fillers

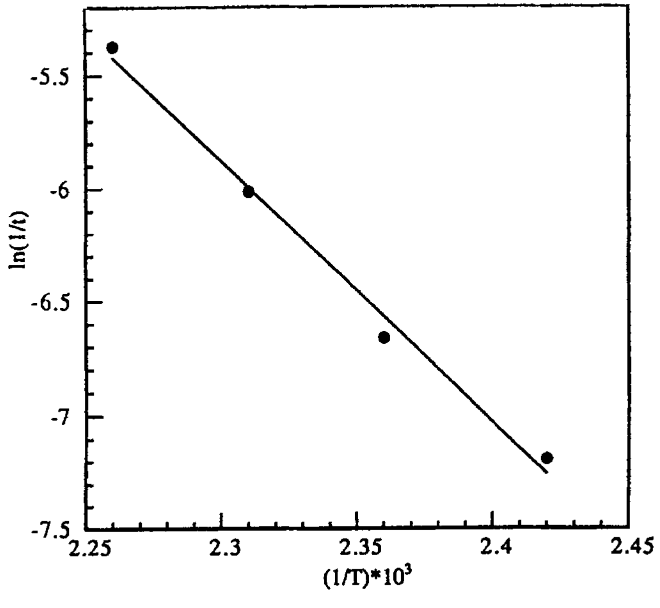

Fig. 8 IDSC results fitting for PBB-MA polymerization on $Mg(OH)_2$ (60% PBB-MA/40% $Mg(OH)_2$)

Figure 6 shows that the polymerization enthalpy also depends on the filler load and on the chemical nature of the filler. The activation energy of the process can be calculated from the results of isothermal analysis [19]. The IDSC method allows study of the kinetics of the polymerization process. Figure 7 shows the IDSC curves of PBB-MA polymerization at different temperatures. One can see that the exothermic polymerization peaks change with temperature. The induction period and the reaction time decrease with increasing temperature. The IDSC results were fitted by the Arrhenius equation.

$$\frac{1}{t} = A\exp\left(-\frac{E}{RT}\right)$$

where t is the polymerization starting time, T is the approximate polymerization starting temperature, E is the apparent activation energy and A is the pre-exponential factor.

The process of PBB-MA polymerization on the surface of fillers can be described by the Arrhenius equation (Fig. 8). The apparent activation energy of the process depends on the filler load and the chemical nature of the filler (Fig. 9). Calculation of this energy shows that the values of E are 83.6–146.3 kJ mol^{-1}, meaning that the process is chemically activated and it is not limited by diffusion processes.

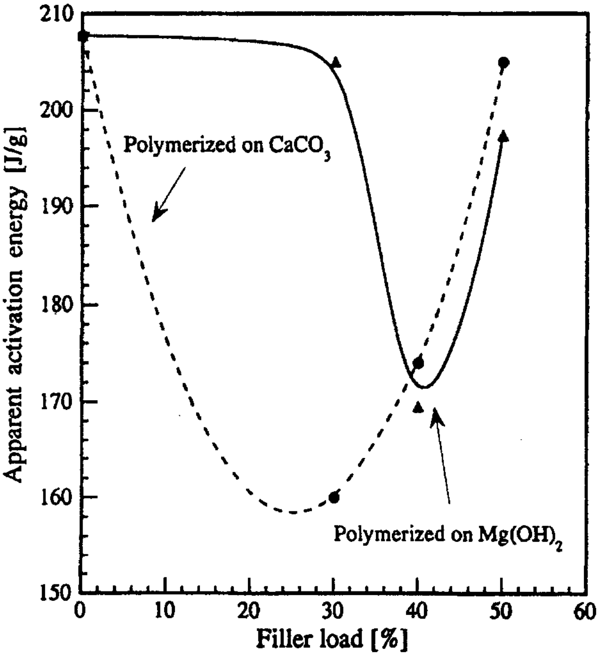

Fig. 9 Apparent activation energy of polymerization on fillers as a function of the filler content

Conclusions

It was shown by FTIR and by extraction methods that the thermal polymerization of flame-retardant monomers on fillers is accompanied by the polymer grafting onto the untreated surface of inorganic particles. Thermal analysis demonstrated that the polymerization on fillers starts at a higher temperature and has lower values of apparent activation energy (at least for moderate filler loads) than polymerization without fillers. The differences in polymer mass loss, polymerization starting temperature, polymerization enthalpy and apparent activation energy when different fillers were added confirm the assumption of the presence of chemical bonding between polymer and filler surface.

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