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NEW APPROACH TO FILLED POLYMERS*
Mechanopolymerization on fillers

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Abstract

Mechanopolymerization of pentabromobenzyl (mono)acrylate (PBB–MA) on the surface of inorganic fillers $Mg(OH)_2$ and $CaCO_3$ was studied. The role of activated surface of fillers was investigated using DSC and FTIR. The influence of milling time and of the filler chemical content on polymerization starting temperature and polymerization enthalpy was studied using DSC. It was shown that an increase of the filler concentration leads to a higher maximum conversion degree. The correlation between conversion kinetics and polymerization enthalpy of the material notpolymerized during milling was shown.

Keywords: fillers, FTIR, mechanopolymerization, milling, thermal analyses

Introduction

Inorganic fillers are often used as additives for polymer matrix [1–3] . They enhance mechanical and thermomechanical properties of plastics. For these purposes an inorganic filler can be mixed with a polymer or a monomer can be polymerized on the surface of a filler. [4–5]. Polymerization on fillers gives the possibility of increasing the impact energy of plastics. Usually polymerization on fillers occurs in extruders under the combined action of the temperature and high shear stresses. However, there is a problem of production of high filled polymers because the usual extruders can not treat high filler concentrations. In this work we suggest a new approach for polymerization on a filler – namely, mechanopolymerization in the planetary milling machine. This approach allows treating of high filler concentrations.

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The processes of polymerization on a filler in an extruder were recently studied [5–6]. Grafting of a polymer onto untreated filler surface indicates that a better adhesion between polymer and filler was achieved. The results of the study of mechanopolymerization of pure monomer indicate the possibility of polymerization during milling [7–12]. The importance of investigating the mechanopolymerization on fillers may be due to the fact that the active surface of the fillers can serve as an additional initiator of the polymerization process. This may be due to formation of the free radical on the new surface formed during the cleavage of filler particles [13]. Therefore an addition of inorganic filler can lead to the polymer grafting onto the filler surface and to the higher yield of conversion. This work is the first one in the study of mechanopolymerization on the surfaces of inorganic fillers.

Experimental details

In this study all the experiments were carried out with the crystalline monomer pentabromobenzyl (mono)acrylate (PBB–MA) ($C_{10}H_5Br_5O_2$) (ex. Dead Sea Bromine Group) which transforms to poly(pentabromobenzyl acrylate) (PBB–PA) during polymerization and which is known to be a flame–retardant [14]. PBB–MA is a white powder with 71.8% of bromine and melting temperature 122°C. Crystalline $CaCO_3$ and $Mg(OH)_2$ with untreated with coupling agents surfaces and average particle sizes 1.5 μm were used as inorganic fillers. Mechanopolymerization occured during milling of the monomer/filler mixture in a 'Fritsch' planetary milling machine at the same velocity (800 rotations per minute) and at different times. Ceramic balls of a 10 mm diameter were used. The conversion degree was tested by FTIR method using a Perkin Elmer 16 PC spectrometer. DSC thermoanalytical curves were recorded on a Mettler DSC 20 calorimeter. The thermoanalytical curves were applied to determine the influence of the milling time and the content of inorganic fillers on polymerization parameters such as starting temperature and enthalpy. The heating rate was 10°C min^{-1} in all the DSC studies. From the DSC curves important information can be deduced about the approximate starting temperature and the enthalpy of polymerization of the material which was not polymerized during the milling. Approximate starting temperature can be observed directly on the plot of thermoanalytical curves by the observable deviation from the base line [15]. The polymerization enthalpies were calculated from the areas under the DSC curve, i.e. per mass of the material which was not polymerized during the milling (after correcting for the polymeric, non-polymeric and filler content).

Results and discussion

The influence of the milling time and the chemical content of the filler on mechanopolymerization kinetics is shown in Fig. 1. It was shown that the addition of $Mg(OH)_2$ increases the conversion degree of the monomer. This means that the activated surface of $Mg(OH)_2$ behaves as an additional polymerization initiator. However, after a long milling time, the processes of mechanodegradation of polymer dominate leading to the lower amount of polymer. By analogy with the thermal decomposition of PBB–PA [16] we may assume that mechanodestruction of the polymer molecule proceeds by pentabromotoluene formation with a probable rupture of C–O bond. It is important to note that the maximum conversion degree increases with an increase of $Mg(OH)_2$ content and that the maximum conversion degree is achieved after one hour of milling. Thus, one hour of milling is an optimal milling time when $Mg(OH)_2$ is used as a filler.

Another filler, namely $CaCO_3$, behaves differ. An addition of 20% of $CaCO_3$ to the monomer leads to almost the same conversion degree as in the case of 20% $Mg(OH)_2$. However, after a long milling time, the amount of the polymer does not decrease. One can assume that the particles of $CaCO_3$ can be cleaved after long milling times. New defects on the surface of $CaCO_3$ can be induced after high milling times as well [17]. Therefore, even after high milling times new polymerization initiators can be obtained on the $CaCO_3$ surface. So, the amount of mechanodegradated polymer and the amount of polymer created during graft–polymerization on $CaCO_3$ surface are nearly the same. If the surface of the milled $CaCO_3$ behaves as polymerization initiator, then an increase of $CaCO_3$ concentration will lead to the higher conversion degree after long milling times. Indeed, as it is shown in Fig. 1, that an addition of 50% of $CaCO_3$ leads to the formation of 70% polymer after 22 h of milling.

Because of the high amount of the non-polymerized material left after milling it was interesting to study the influence of mechanical activation and filler content on the thermal polymerization of the non-polymerized material. Figure 2 shows an influence of the milling time and filler content on the polymerization

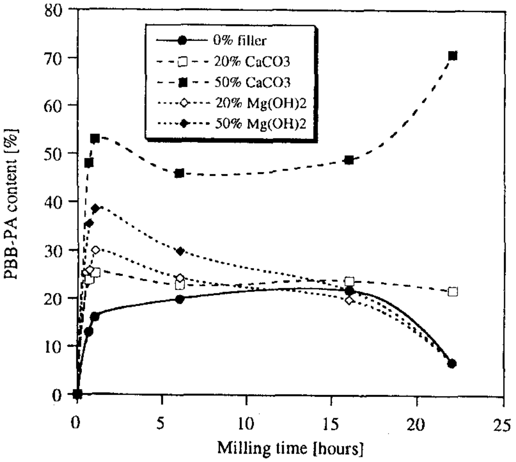

Fig. 1 Polymer (PBB–PA) amount as a function of the milling time and the chemical content of mineral filler

starting temperature. At time t=0 one can see an influence of inorganic filler on the polymerization starting temperature of unmilled monomer. The addition of inorganic fillers increases the polymerization starting temperature. This can be explained by the differing thermal capacities of the fillers and the monomer. The increase in this difference during the low milling times can be explained in the following manner: the energy absorption by crystalline monomer and filler is different; in both materials such absorption will lead to mechanically induced defects which increases the heat capacity of material [18]. So, the different absorption of mechanical energy will lead to a difference in the amount of mechanically induced vacancies and therefore to the higher difference between heat capacities after the low milling times. At long milling times an active surface of filler behaves as a polymerization initiator and the polymerization starting temperature will decrease. It seems that the polymerization starting temperature has to decrease after longe milling times and high filler concentrations. The curves for 50% fillers in Fig. 2 confirm this assumption.

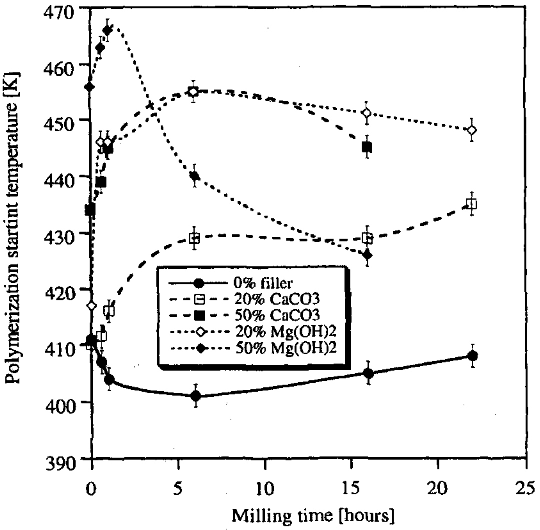

Fig. 2 Polymerization starting temperature of the material non-polymerized during milling as a function of the milling time and the chemical content of mineral filler

An influence of milling time and filler content on polymerization enthalpy of the material which was not polymerized during milling is shown in Fig. 3. One can see a decrease of polymerization enthalpy when $Mg(OH)_2$ is added. This decrease can be explained as follows: during mechanopolymerization, a high conversion degree is reached (Fig. 1). This leads to high concentrations of destructed polymer formed after mechanodegradation process. Taking into account the fact that polymerization enthalpy is the sum of the exothermal effects from each elementary stage of a reaction, one can conclude that the high amount of oli-

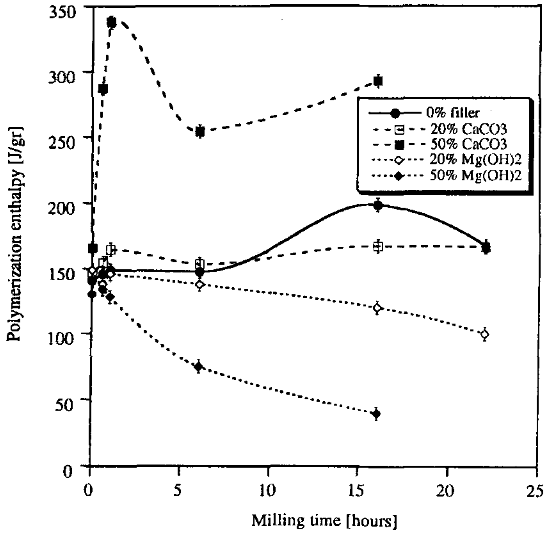

Fig. 3 Polymerization enthalpy of the material non-polymerized during milling as a function of the milling time and the chemical content of mineral filler

gomers will cause a decrease of the polymerization enthalpy as calculated per gram of non–polymerized material. The amount of the products of polymer distraction increases with the milling time, therefore, the polymerization enthalpy decreases. However, one can see from Fig. 1 that mechanodestruction is less significant when $CaCO_3$ is used as the filler and the polymerization on the filler surface is a more dominant process. The polymerization enthalpy of a non-polymerized material must be higher when $CaCO_3$ is added rather $Mg(OH)_2$. In addition, the polymerization enthalpy should not decrease by increasing the milling time when 20% $CaCO_3$ is added, and it must increase after a long milling time when 50% $CaCO_3$ is added. This assumption is confirmed by the curves in Fig. 3.

In light of the above arguments, and the fact that the polymerization enthalpy of unmilled monomer is higher when 50% $CaCO_3$ is added, in comparison with the addition of 50% $Mg(OH)_2$ (as evidenced at $t=0$), one can explain the total increase of polymerization enthalpy of the material which was not polymerized during the milling in the case of $CaCO_3$ addition.

After more than 16 h of milling of the mixture with 50% of fillers, the DSC curve was changed dramatically and it was not possible to calculate the polymerization parameters.

Conclusions

This study indicates that it is possible to achieve a high concentration degree during mechanopolymerization when an inorganic filler such as $CaCO_3$ is added.

It makes the process of mechanopolymerization a more convenient technology for polymerization on fillers in comparison with an ordinary reactive extrusion process. The maximum conversion degree is different for different fillers content. The time for maximum conversion degree also differs for different fillers. Methods used for thermal analyses are also useful for mechanopolymerization study. There is a correlation between FTIR data regarding the conversion kinetics and the thermodynamic parameters obtained using DSC.

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