Solid-Phase Functionauzation of Isotactic Polypropylene with Maleic Anhydride. Influence of Solvents and Additives on the Level of the Reaction

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SOLID-PHASE FUNCTIONALIZATION OF ISOTACTIC POLYPROPYLENE WITH MALEIC ANHYDRIDE. INFLUENCE OF SOLVENTS AND ADDITIVES ON THE LEVEL OF THE REACTION

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ABSTRACT

Radical reaction between isotactic polypropylene and maleic anhydride initiated by peroxide at temperatures lower than the melting point of the polymer in the absence of liquid medium in the solid phase was studied. It was found that conversion of the reaction in the case of

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mixing of reagents into a pulverized polymer by the impregnation method is satisfactory in comparison with reaction conversion in the melt. It was found that reaction conversion in the solid phase can be increased up to 30% in the presence of a small amount of an organic solution, such as xylene (5 to 10%).

INTRODUCTION

A few years ago the method of functionalization of powder isotactic polypropylene (iPP) in the solid phase with maleic anhydride (MAN) at a temperature below the melting point [1] was developed. We returned to this field of study mainly because of general interest in new, efficient procedures of functionalization of iPP with MAN. This interest is due to the fact that functionalization of iPP with MAN is a very efficient way of increasing the polarity of iPP. Modified iPP can be used for significant improvement of the mechanical properties of composites of iPP (mainly with inorganic fillers such as MgO, glass, metal) [2–5] and blends with polar polymers (for instance, polyamides) [6, 7].

Functionalization of powder iPP with MAN can be evaluated as a solid-phase reaction only from the macroscopic point of view. In fact, under the reaction conditions MAN and peroxide are in liquid form and are able to diffuse in particles of iPP, but iPP remains in the powder form after the reaction, which seems to be an advantage from the point or view of application.

Reagent diffusion probably takes place mostly in the upper layers of iPP particles and mainly in the amorphous part of the polymer.

Several reaction mechanisms were suggested for the functionalization of iPP [8–10]. It is generally accepted that these reactions can be initiated by peroxide radicals after a transfer reaction to the polymer results in polymer radicals. Polymer radicals, as reaction centers binding MAN, can also be obtained by thermomechanic destruction of the polymer, mainly in the case of binding MAN to unsaturated polymers (for instance, polydienes) [11]. The efficiency of the functionalization reaction depends only on the efficiency of the addition reaction of the polymer radical on the double bond of MAN under reaction conditions used. It is not clear yet whether, after addition of one monomer unit of MAN, the addition of other units of MAN to the MAN radical formed takes place. Both possibilities have been suggested: formation of short side MAN chains [8] as well as binding of separate monomer units [12], the presence of which has been proven by experiments in model studies of binding MAN to *n*-eicosane [13] and to iPP [14].

It was found that certain solvents (e.g., toluene) in small amounts (up to 10%) increase conversion of the solid phase reaction. The ability of the solvent to etch and swell the polymer surface was attributed to an increase in functionalization levels [15].

In this paper we compare the level of functionalization of iPP below and above the polymer melting point. We follow the influence of the concentrations of initiator and MAN on the functionalization level. Our main attention was devoted to the influence of solvents and additives on the functionalization level.

EXPERIMENTAL

Reaction of Maleic Anhydride with Isotactic Polypropylene

We used unstabilized pulverized isotactic polypropylene type HPF obtained from Slovnaft. This polymer had an average molecular mass of 200,000 g/mol. The reactants were mixed with pulverized iPP using an impregnation method. Pulverized iPP (1 to 2 g) was impregnated in an etheric solution (20 mL) containing t-butyl perbenzoate (3 wt% by mass of reaction mixture) and maleic anhydride (1 to 8 wt% by mass of iPP). The mixture was stored in the dark for 24 hours. Then ether was removed by vacuum evaporation and the sample was sealed in a glass tube under nitrogen. The reaction of iPP with MAN was initiated by peroxide by curing the sample at the required temperature and a reaction time corresponding to 6 half-times of t-butyl perbenzoate. After the reaction, unreacted reagents, such as low molecular weight reaction products, were removed by extraction in boiling acetone for 1 hour. The sample was dried in a vacuum drier to constant mass.

Determination of Maleic Anhydride in Modified Isotactic Polypropylene

The quantity of bound MAN in iPP after reaction and extraction was determined according to titrimetry as described by Gaylord [16]. We used about 0.5 g of the sample dissolved in water-saturated xylene, and the solution was titrated using 0.02 N KOH in n-butanol solution to a phenolphthalein endpoint.

Thermogravimetry of Functionalized Isotactic Polypropylene with Maleic Anhydride

The thermogravimetry course of decomposition of functionalized iPP samples with maleic anhydride after removal of low molecular reaction products by extraction in boiling acetone and of the original iPP were determined on a Perkin-Elmer thermobalance (TGS-1) with a 3-mg sample at a flow of 60 L/hour of N_2 for nonisothermal experiments (heating rate 10 K/min) (Fig. 1).

IR Spectrum of Functionalized Isotactic Polypropylene

The IR spectrum of a functionalized iPP film after removal of low molecular reaction products by extraction was recorded by a Specord M 80 IR apparatus (Carl Zeiss, Jena). A very strong absorption near 1780 cm^{-1} was found (Fig. 2).

RESULTS AND DISCUSSION

Thermogravimetric measurements of functionalized isotactic polypropylene with maleic anhydride (Fig. 1, Curves 1 and 2) don't show any weight changes from
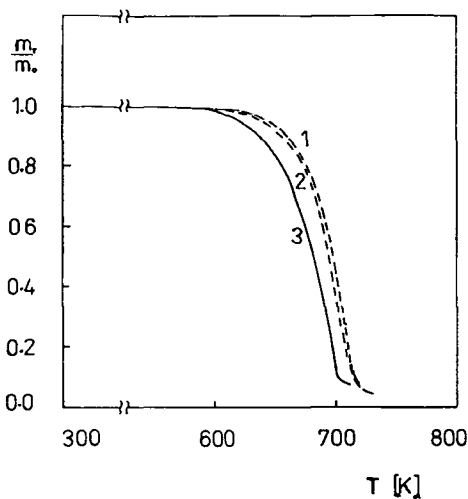
FIG. 1. Thermogravimetry curves of functionalized isotactic polypropylene with 1.27% of bound maleic anhydride groups (Curves 1 and 2, reproducibility of the same sample) and isotactic polypropylene alone (Curve 3).

300 to 600 K. That means that after extraction with acetone, this functionalized polymer does not contain any low molecular weight compounds. The better thermal stability of the functionalized polymer in comparison with iPP alone (Fig. 1, Curve 3) can be accounted for by reaction of double bonds or other anomalous and reactive groups containing iPP with maleic anhydride during the functionalization reaction.

The IR spectrum of functionalized iPP (Fig. 2) shows a very strong absorption near 1780 cm^{-1} which belongs to C=O stretchings of the succinic anhydride.
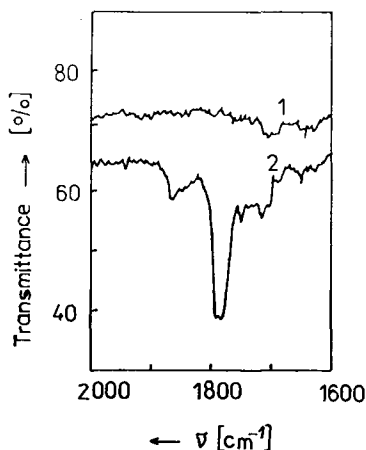

FIG. 2. Infrared spectrum of isotactic polypropylene alone (Curve 1) and functionalized isotactic polypropylene with 1.27% of bound maleic anhydride groups (Curve 2).

The influence of MAN concentration at a constant concentration of *t*-butyl perbenzoate (TBPB) in the reaction blend on the total content of MAN bound to the PP chain after reaction is shown in Fig. 3. Dependence 1 shows the case when reaction took place in the melt under static conditions (at 180°C). Dependence 2 reflects a temperature lower than the melting point of the polymer (150°C), i.e., at solid phase conditions. For measuring both temperature dependences, the reagents were mixed into iPP in equal amounts by the impregnation method described in the Experimental Section. For reaction temperatures of 150 and 180°C, the dependence of the degree of grafting of MAN on the concentration of MAN in the reaction mixture is surprisingly similar up to 4% MAN. In this region the difference of binding of MAN is minimal although the difference in reaction temperature is 30°C. This low difference can be explained mainly by the fact that the impregnation method of preparing the reaction mixture does not allow a uniform dispersion of reagents in the iPP powder particles. Reagents can be practically dissolved only in the amorphous part of the polymer. This means that the low temperature reaction will involve a higher concentration of reagents (MAN and peroxide), and they react in the amorphous part of the iPP particles. This compares favorably with the high temperature reaction in which the reagents are somewhat more absorbed and diluted by the polymer.

The reduction of the amount of bound MAN, starting at a content of about 5% MAN and a reaction temperature of 150°C and at a content of 6% MAN in the reaction mixture and a temperature of 180°C, can be caused by different factors. One of them could be the higher participation of reagents; that is, peroxide and MAN in mutual reaction in comparison with lower concentrations of MAN. This lowers participation of the transfer reaction of radical initiator onto the polymer, which is of highest importance for the functionalization reaction. Later, at a higher
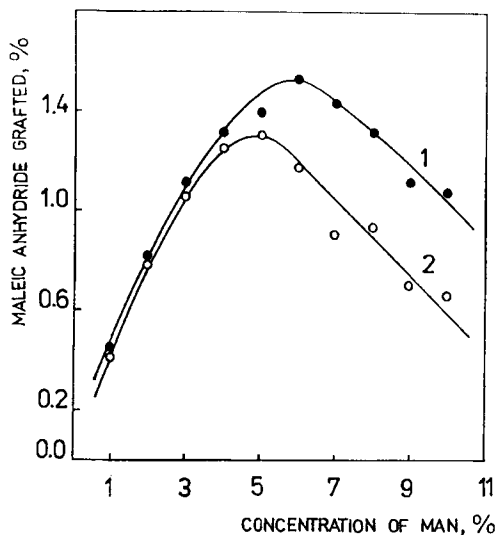

FIG. 3. Effect of maleic anhydride–MAN concentration on the functionalization level (3 wt% *t*-butyl perbenzoate): Curve 1, at 180°C; Curve 2, at 150°C.

concentration of MAN, the amorphous part of the polymer is unable to accept more MAN. Then the amount of MAN remaining on the surface of iPP particles is increased and can not take part in the functionalization reaction.

The influence of TBPB concentration on binding MAN to iPP at constant MAN content (4%) of the reaction mixture at a temperature below the melting point of polymer is shown in Fig. 4. A noticeable increase of bound MAN can be observed only up to 4% TBPB. A further increase in peroxide content leads to only a small increase of bound MAN; at 6%, TBPB leads to the formation of an insoluble gel, which implies that crosslinking of the polymer is occurring. The lower increase of bound MAN in Fig. 4 at concentrations higher than 4% TBPB is caused by the fact that it is only the concentration of polymer radicals that increases, not the concentration of MAN.

The conversion of the reaction of pulverized iPP with MAN at temperatures below the melting point of the polymer in the presence of small amounts of various additives or solvents was studied. Figure 5 shows the dependence of conversion of the iPP with MAN reaction on the concentrations of different solvents. Tridecane, dioctyl phthalate, xylene, and ethyl stearate increase the reaction conversion slightly less (10 to 20%). Figure 6 shows the dependence of the reaction conversion on the reaction temperature at constant concentrations of peroxide, MAN, and additive (5%). The observed dependences prove that the additives are most efficient in producing functionalized iPP with MAN at low temperatures (from 110 to 130°C). In this region the relative increase of bound MAN is about 30% for a reaction temperature of 110°C.

The positive influence of additives on the grafting yields can be explained by an improved transport of reagents into the amorphous phase of the polymer in the presence of additives. Also, the solubility of reagents in a partially swollen polymer
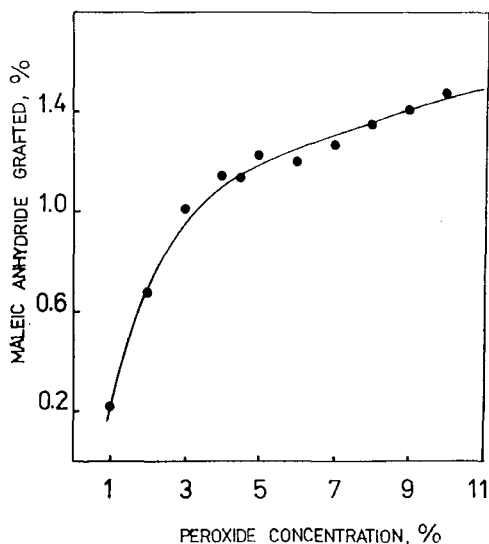

FIG. 4.   Effect of *t*-butyl perbenzoate on maleic anhydride–MAN functionalization level (4 wt% maleic anhydride, 150°C).
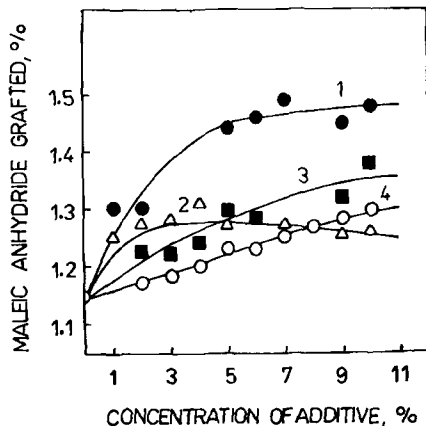
FIG. 5. Effect of additives on the maleic anhydride functionalization level at 150°C (3 wt% *t*-butyl perbenzoate, 4 wt% maleic anhydride): Curve 1, tridecane; Curve 2, ethyl stearate; Curve 3, dioctyl phthalate; Curve 4, xylene.

in the presence of additive should be easier. We believe that additives, like solvents, enable a better distribution of functionalization reagents in the amorphous phase of the polymer. With a better distribution of reagents in the polymer, undesirable competitive reactions, such as the direct reaction between peroxide and MAN, can be minimized. Therefore, we can expect an increase in the efficiency of reaction of reagents with polymer [15].
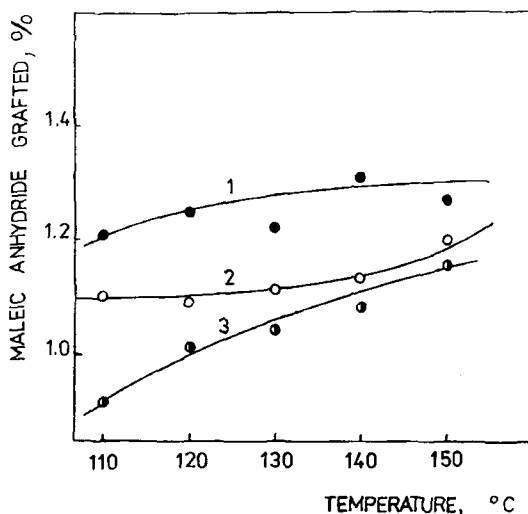

FIG. 6. Effect of additives (5 wt%) on maleic anhydride functionalization level at various temperatures (3 wt% *t*-butyl perbenzoate, 4 wt% maleic anhydride): Curve 1, ethyl stearate; Curve 2, dioctyl phthalate; Curve 3, without additives.

CONCLUSIONS

By studying the functionalization of iPP with MAN in the solid state under specific reaction conditions and procedures, it was found:

1. The reaction of iPP with MAN initiated by peroxide at a temperature below the melting point of the polymer (150°C) is quite effective in comparison with reaction in the melt. No significant differences were found in the quantity of bound MAN.
2. Conversion of the functionalization reaction at a temperature below the melting point of the polymer can be increased by 30% when small amounts of additives, such as solvents, are used.

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