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POLYPROPYLENE, MODIFIED WITH SOME OLIGOESTERS

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Abstract: Miscibility of polypropylene with some oligoesters was evaluated by optical wedge interference microscopy. Mechanical, thermal, rheological and relaxation properties were studied. Compatibility between the polymers and modifying agents was shown to have a marked effect on stress-strain properties as well as on the structure and melting characteristics of the modified polymers.

INTRODUCTION

Modification of the commercial polymers with minor amounts of some other polymers and oligomers is widely used for the preparation of polymeric materials with enhanced properties. However the mechanism of this betterment is still unclear. It has been known that stress-strain properties of polymers may improve with incorporating of incompatible additives (Ref. 1). Also enhances of polymers characteristics were noted with introducing of compatible oligomers or other polymers (Ref. 2). At the present time, no universal standpoint, concerning the optimal phase composition of polymeric composite materials is available. In this work we studied the effect of various oligoesters on the structure and properties of polypropylene.

RESULTS AND DISCUSSION

Materials

A commercial sample of polypropylene trade name "Kaplen" 01030, oligoesters based on phtalic acid (DAF), sebaic acid (DOS) and adipic acid (PDA) were used in this work.

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Methods

Rheological properties of modified PP were studied in this work by capillary viscometry using an MV-2 viscometer at temperatures from 200 to 250 °C.

Thermal parameters of PP (Melting points Tm, melting heat ΔH) were determined by DSC using Du Pont thermoanalyzer TA-912. Experiments were performed at a constant heating rate of 5 k/min.

Dynamic properties were measured by a free damping oscillation method using a standard frequency of the order of 1 Hz.

For the purpose of studing the interaction between PP and modifiers the optical wedge interference micromethod was used (Ref. 3). This method is based on multipath interference from the polymer plate surfaces. When swelling of oligoesters begins, the process manifests itself in the appearance of the curved interference bands in the vicinity of interfacial boundaries. With increasing temperature, the number of such bands increases, i.e., solubility increases. Finally, complete disappearance of interfacial boundaries is observed, that is, dissolution of PP in modifier is accomplished. This implies that the interference bands of oligoester are gragually transformed into the bands of polypropylene. At different temperatures the concentration of oligoester additives dissolved in PP matrix and concentration of PP dissolved in oligoesters was determined; and diagrams of state were constructed (Fig. 1).

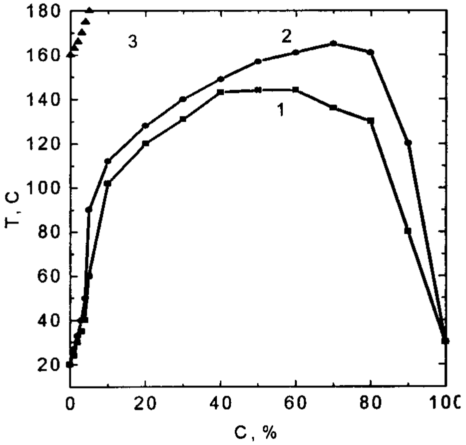

Fig. 1. Phase state diagrams for (1) PP - DOS, (2) PP - DAF, (3) PP - PPA.

The corresponding diagrams of state allow estimation of upper critical solution temperatures (UCST). For the PP-DOS system UCST is equal to

145 ^{0}C, whereas for PP-DAF to 165 ^{0}C. The system PP-PPA is almost incompatible in the studied range of temperatures.

Rheological properties of modified PP were studied at temperatures from 200 to 250 ^{0}C. For initial and modified blends flow curves were obtained. With increasing the content of oligoesters in PP, the flow curves are shifted towards higher shear rates, and this behavior is explained by a decrease in melt viscosities.

When a low-viscous oligomeric additive is added to a polymer melt the viscosity of polymer melt monotonously decreases with an increase in oligoester content (Fig. 2).

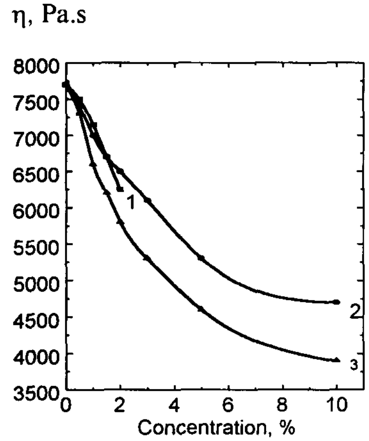

Fig. 2. Melt viscosity of PP compositions vs. content of oligoesters in PP: (1) PPA, (2) DAF, and (3) DOS.

For PP compositions, bearing PPA and DOS activation energies for viscous flow E_a were estimated from the corresponding temperature dependences of melt viscosity. The values of E_a are presented in Table 1.

Tab. 1. Activation energies for viscous flow.

Composition	PP	PP+1% PPA	PP + 2% PPA	PP + 3% DOS	PP + 5% DOS	PP + 10% DOS
E_a, KJ/mol	31	29	27	29	28	22

Incorporating of oligoesters cause the values of E_a to decrease independently on the compatibility between the polymers and the modifying additives. Increasing the oligoesters content decreases activation energy for viscous flow values.

Thermal characteristics of the compositions are presented in Table 2.

Tab. 2. Melting points T_m, melting heat values ΔH and melting temperature ranges ΔT of PP compositions.

Composition	ΔT, ^{0} C	T_m, ^{0} C	ΔH, KJ/mol
PP	108-175	166	84
PP + 3% DAF	122-172	162	79
PP + 5% DAF	125-174	163	72
PP + 2 % PPA	120-169	166	87
PP + 5% PPA	125-174	163	84

Incorporating of compatible on a limited scale additives DOS and DAF cause the decrease of the degree of crystallinity of PP.It decreases as the modifiers concentration is increased. Introducing PPA into PP in minor amounts causes an increase of degree of crystallinity. The PP crystallinity dependence on PPA concentration passes through maximum.

The melting point of PP is almost unaffected by oligoesters, though melting temperature range narrows on addition of all modifiers independently of their compatibility with PP.

Incorporating oligomers influence not only PP structure, but their stress-strain properties as well. Polypropylene tensile strength σ_t and breaking strain ε dependences versus PPA content pass through maximum in the range of PPA concentration of 1-2wt.%. This concentration region is characterized by maximum degree of crystallinity also.

On addition of compatible at high temperatures DAF and DOS tensile strenth decreases monotonously and breaking strain passes through maximum in the range of oligomers concentration 5-7 weight%. These results are in agreement with crystallinity changes: the decrease of crystallinity causes σ_t decrease and ε increase. Dynamic shear modulus of PP decreases when oligomer content increases (Fig. 3). Also breaking strain increase may be caused by PP chain mobility enhancement in the presence of additives. During crystallization modifiers are displaced to amorphous imperfect regions. The surface boundary of polymer-incompatible additive may act as nucleus (in the case of PP-PPA system). Unmiscible additives lokate in polymer amorphous defect zones and induce expansion of polymer free volume. Chain mobility increase in the oligomers presence may cause crystallization rate growth. Relaxation properties accelerate, polymer structure turns to be more regular and mechanical properties grow. On further increase of oligoesters content they begin to screen off the growing sphrerulites surfaces and to inhibit crystallization. Compatibility of polymer and modifier influence greately on the structure and also on the properties of the materials obtained..

The increase of chain mobility of modified PP is showed by dynamic mechanical analysis (Fig. 4).

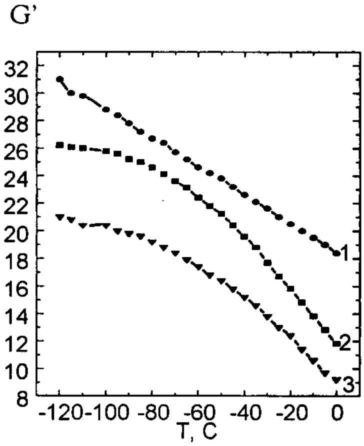

Fig. 3. Shear modulus dependence vs temperature: (1) PP, (2) PP + 5 weight% DAF, and (3) PP + 10 weight% DAF.

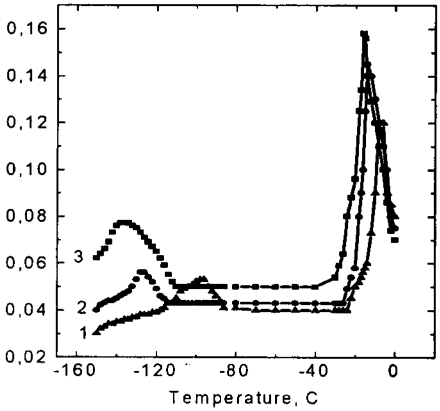

Fig. 4. Loss tangent dependence vs temperature: (1) PP, (2) PP + 5 weight% DAF, and (3) PP + 10 weight% DAF.

CONCLUSION

The influence of different oligoesters on the structure and properties of PP was studied. It was shown, that miscibility between PP and the modifiers has a marked effect on stress-strain properties as well as on the structure and melting characteristics of the modified polymers.

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PREVIOUS PUBLICATIONS

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