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Apparent compatibility in *n*-alkane/poly(dimethyl phenylene oxide) blends

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SUMMARY

We report here on the apparent compatibility of a series of *n*-alkane/PDMPO blends. Three alkanes were examined [eicosane (C_{20}), tetracosane (C_{24}), and Polywax 2000 (nominally C_{142})] as blends of 5, 10, 15, and 20 wt.% alkane with PDMPO. Samples were judged to be compatible or incompatible according to three criteria: (a) visual appearance, i.e., transparent vs. opaque molded specimens, (b) the presence or absence of an alkane crystalline melting peak in a DSC thermogram, and (c) downward shifts in the PDMPO-rich phase glass transition temperatures from the T_g range of 195-200°C for PDMPO homopolymer. The $T_u > T_m$ alkane component transition has not been observed in any of the blends prepared to date.

INTRODUCTION

A number of reports have appeared in the literature discussing the $T_u > T_m$ transition in linear alkanes and semicrystalline polymers (1-7). A discussion by one of us (SEK) with Kruger (8) led us to investigate the potential T_u characteristics of a series of linear alkanes using dynamic mechanical analysis (DMA). To our knowledge, no one has published DMA results on the T_u transition phenomenon other than us (9), and that report mentioned only one polymer in passing, viz., gutta percha.

In order to study "soft" materials by DMA, i.e., amorphous polymers above T_g or semicrystalline polymers above T_m, one has to support the sample of interest via an inert matrix of one sort or another. The perforated shim stock method is one approach (9). In this technique, the material of interest is coated onto an inert, usually metallic support. An alternative technique involves polymer blend encapsulation (10). Here, the polymer of interest is blended as a minor component with another polymer, preferably having a high T_g and being incompatible with the polymer under evaluation.

In this report, we present some preliminary results of our investigations of *n*-alkane/PDMPO blends, the alkane component being present as the minor phase in all cases.

The application of the polymer blend encapsulation technique to study the alkane phase T_u transition in this system proved to be infeasible. T_u transitions were not observed in any of the blends examined to date as a result of the confounding effect of apparent compatibility between PDMPO and the lower *n*-alkanes, in particular. The observed glass transition temperatures of the PDMPO-rich phase were shifted down into the range where the alkane component T_u transitions would have been expected to appear, and frequently the alkane phase was notably absent.

Thus, the emphasis of this communication will be on the thermal transition characteristics and visual appearance of various *n*-alkane/PDMPO blends.

EXPERIMENTAL

Eicosane (C_{20}), tetracosane (C_{24}), and Polywax 2000 (nominally C_{142}) were blended with poly(2,6-dimethyl-1,4-phenylene oxide) (PDMPO). This polymer was chosen for it's high T_g and relatively transition-free flat damping background in DMA tests. The materials were used as recieved from the suppliers (see Table 1). The physical form of the eicosane and tetracosane samples was waxy white flakes. Polywax 2000 was in the form of hard waxy beads and PDMPO was a fine powder of general molding grade resin. Reagent grade *p*-xylene was used as the freeze drying solvent medium.

The polymer blends were prepared by a solution blending/freeze drying method. For each of the two alkanes and Polywax sample used, 5, 10, 15, and 20 weight percent blends were prepared for a total of 12 blends. The combined dry weight of each blend was

Table 1. Materials.

Name	Formula	T_m (°C)[a]	Source
Eicosane	$C_{20}H_{42}$	43.4	Aldrich
Tetracosane	$C_{24}H_{50}$	53.0	Aldrich
Polywax 2000	$C_{142}H_{286}$[b]	128.6	Bareco
PDMPO[c]	$-(C_6H_2(CH_3)_2O)_n-$	d	G. E.

(a) Melting points determined by DSC.
(b) Nominal composition.
(c) Poly(2,6-dimethyl-1,4-phenylene oxide).
(d) Noncrystalline polymer, T_g = 195°C by DSC.

approximately six grams. The weighed mixture of PDMPO and alkane was placed into an 8 oz. wide mouth sample jar with 100 ml of *p*-xylene. The sample bottle was covered with a watch glass and heated to approximately 75-80°C to aid dissolution of both components and the sample mixture was kept at that elevated temperature until all of the solid material had dissolved. The temperature was then lowered to 60°C and the solution was maintained at this temperature for at least 15 hours to assure homogeneous blending of the two components.

After the solution blending operation, the sample bottle was placed into a crushed ice bath to cool it below *p*-xylene's freezing point (m.p. 13°C). Care was taken to rotate the bottle during freezing so that a shell of the alkane/PDMPO/*p*-xylene mixture formed on the walls of the bottle, maximizing the surface area. The sample was placed into a bed of crushed dry ice for approximately one hour to ensure complete freezing. When the solution was fully frozen it was dried on a Labconco bench top freeze dryer (Model No. 75035). Each sample was evacuated for one to two days to near dryness. The removal of any resdiual *p*-xylene was accomplished by placing the samples in a vacuum oven at approximately 80°C for an additional one to two days.

The resultant freeze dried foams were compression molded using a Pasadena platen press. Approximately 2.7 grams of the powdery foam was pre-compacted at room temperature and then placed into a 2" x 2" x 0.04" mold. The mold assembly was first placed into the preheated press (250°C) for three minutes under no pressure, and then a pressure of 2,500 psi was applied for three minutes. The press was subsequently cooled to near room temperature by passing cold water through the platens while maintaining the mold under pressure.

Differential scanning calorimetry (DuPont 912 DSC) was performed on the molded specimens. Samples of approximately 15-20 mg were heated in hermetically sealed sample pans from room temperature to 250°C at 10°C/min under a nitrogen purge (20 cc/min). The DSC cell was cooled after the first heat using the DuPont DSC cooling can accessory and a second heat was performed under the same conditions.

The compression molded specimens were cut into samples of approximately 1 cm x 3 cm for dynamic mechanical analysis (DuPont 982 DMA). Samples were mounted in the DMA clamp assembly at a clamping distance of 6.4 mm to 6.7 mm. The thickness dimension from one sample to the next varied from 0.84 mm to 0.96 mm. Sample widths ranged from 1.0 mm to 1.3 mm. An oscillation amplitude of 0.2 mm peak-to-peak and a heating rate of 5°C/min was used for all DMA runs. The temperature range tested was from 0°C to just above the T_g of PDMPO or when the relative damping signal fell below zero. The DMA resonant frequency was approximately five to six hertz around the T_g range for all samples tested.

RESULTS AND DISCUSSION

PDMPO powder, as supplied, gave a T_g of 215°C by DSC, which also was the T_g for the first heats on the homopolymer freeze dried foams. First heats on the molded samples and second heats on the powders gave an average T_g of 195°C. DMA results on the molded specimens gave a T_g of 199°C in good agreement with DSC observations. The agreement between the glass transition temperatures for the different forms of PDMPO (as received, freeze dried, and subsequently molded) suggests that the sample blending method had no deleterious effect on the PDMPO phase.

Table 2 summarizes the optical clarity characteristics of the molded samples. The molded blends of eicosane/PDMPO were transparent, similar to PDMPO homopolymer molded specimens. This was the first indication that eicosane and PDMPO may form a compatible system. DSC thermograms also showed no indication of a melting transition process for the eicosane component in any of the weight percent blends examined. Furthermore, a marked T_g shift was noted for the PDMPO phase, with greater shifts at the higher weight percentages. The glass transition was observed to range from 154°C for the 5 wt.% blend down to 99°C for the 20 wt.% blend (see Table 3).

The tetracosane/PDMPO blends did not follow the same behavior as the eicosane blends over the weight percent range studied. Molded specimens of the 5 and 10 wt.% blends were transluscent while the 15 and 20 wt.% blends were opaque. Differences were also noted by DSC analysis as shown in Figure 1. No alkane melting peaks were observed for the 5 and 10 wt.% blends and a shift in the T_gs indicated that tetracosane and PDMPO were compatible in this composition range. The behavior was different, though, for the 15 and 20 wt.% blends in that a melting transition was found for tetracosane along with a shift in the T_gs. It appeared that

Table 2. Appearance of compression molded blends.[a]

	Wt.% alkane in blend			
Alkane	5%	10%	15%	20%
Eicosane (C_{20})	transparent	transparent	transparent	transparent
Tetracosane (C_{24})	transluscent	transluscent	opaque	opaque
Polywax 2000	opaque	opaque	opaque	opaque

(a) PDMPO homopolymer yields transparent, amber-colored moldings.

Table 3. Glass transition temperatures of compression molded blends by DSC and DMA.[a,b]

	Wt.% alkane in blend							
	5%		10%		15%		20%	
Alkane	DSC	DMA	DSC	DMA	DSC	DMA	DSC	DMA
Eicosane (C_{20})	154	169	131	149	99	114	99	118
Tetracosane (C_{24})	155	167	120	136	108	131	122	137
Polywax 2000	189	192	200	202	192	196	199	198

(a) Glass transition temperatures expressed as °C.

(b) DSC T_gs are averaged values of four to six runs (first and second heats on two to three samples). DMA T_gs are averaged values of two to four runs (first heats only).

two phases may exist in this blend pair at the higher blend ratios, one phase being a compatible mixture of tetracosane and PDMPO, the other, a pure tetracosane phase.

Polywax 2000/PDMPO moldings were opaque for all weight percent blends examined and DSC analysis showed melting transitions for all of the Polywax blends. However, as with the lower alkanes, Polywax 2000 did show a slight shift in the T_g of the PDMPO phase ranging from 189-200°C by DSC.

Dynamic mechanical analysis was used to verify the results obtained by DSC analysis. Figure 2 shows the DMA results for the 15 wt.% samples of the alkane/PDMPO blend series. The DSC thermograms for the 15 wt.% eicosane blend showed no melting transition as confirmed by the DMA trace which showed a flat damping profile up to the lowered PDMPO T_g. The DMA thermogram for the 15 wt.% tetracosane blend showed a small loss peak around 40°C corresponding to the melting peak found in DSC. Here, too, the glass transition of the PDMPO phase is depressed from the expected value of 199°C for PDMPO homopolymer. The DMA thermogram of the 15 wt.% Polywax 2000 blend showed a broad loss maxima corresponding to the melting process of the Polywax phase as expected along with a T_g in good agreement with DSC results. In general, there was good agreement between the glass transition temperatures determined by either DSC or DMA for all of the blends studied (see Table 3).

The DMA thermograms of the 15 wt.% blends in Figure 2 showed no indication of any loss peaks corresponding to the T_u transition of linear alkanes. Using the rule $T_u = 1.2 \times T_m$, as set forth by Boyer et al. (4), the expected T_u loss peaks would be at 106°C for eicosane, 118°C for tetracosane, and 208°C for Polywax 2000. A potential T_u transition was obscured by the onset of the blend T_g for the eicosane and tetracosane systems while Polywax 2000's anticipated T_u was above the T_g of its blends. In fact, none of the blends examined showed any evidence for an alkane phase T_u transition.

CONCLUSIONS

Using our definition of apparent compatibility set forth earlier in this paper we conclude that the eicosane/PDMPO blends are completely compatible over the weight percent range examined to date (5 to 20 wt.% alkane). The four blends of eicosane passed all three criteria: (a) transparency, (b) absence of a crystalline melting transition for eicosane, and (c) a shifted PDMPO-rich phase T_g. Tetracosane and Polywax 2000 met only some of these criteria giving us reason to believe that they are compatible over a more limited compositional range. It appears that these blends form two phases, an alkane rich phase and a compatible phase of

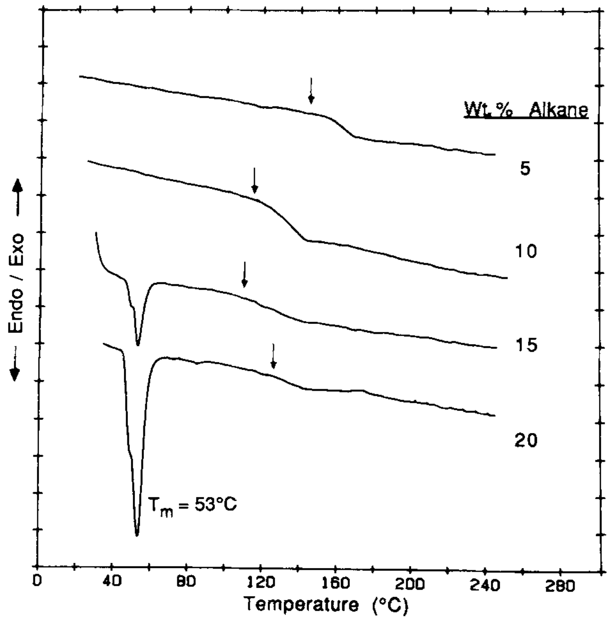

Figure 1. DSC thermograms of the tetracosane/PDMPO blend series. *Y*-axis: heat flow, 1.0 mW/division, individual traces shifted vertically for clarity. Arrows indicate the shifting of the T_g of the PDMPO-rich phase.

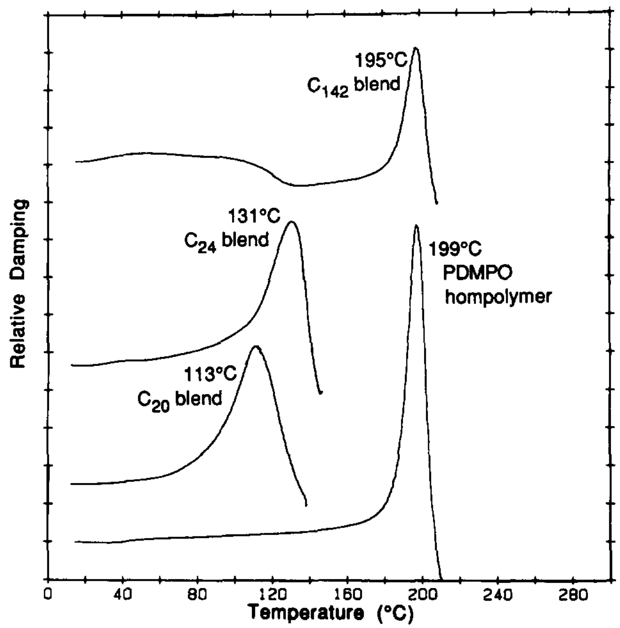

Figure 2. DMA thermograms of a series of *n*-alkane/PDMPO blends, all alkanes present as 15 wt.%. *Y*-axis: 20 mV/division, individual traces shifted vertically for clarity. Resonant frequency range at T_g peak, approximately 5 to 6 hertz for all samples.

alkane and PDMPO. From our initial analysis, it appears that the compatibility range in these materials may be related to the molecular weight of the alkane and the weight percent of alkane added to PDMPO. Finally, due to compatibility considerations, we have not been able to detect T_u transitions in the alkane phase using the encapsulated polymer blend technique with PDMPO.

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