Phenoxy and diglycidyl ether of bisphenol-A as compatibilizers for nylon 6/methyl methacrylate–styrene–butadiene graft polymer blends

Young Soo Soh
Department of Chemical Engineering, Taegu University, Kyungbook, Kyungsan-gun, Jinryang-myun, Korea
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Poly(hydroxy ether of bisphenol-A) (phenoxy resin) and diglycidyl ether of bisphenol-A type epoxy resin (DGEBA) are found to be excellent compatibilizers for polyamide 6 (nylon 6)/methyl methacrylate–styrene–butadiene (MBS) graft polymer blends. When the blends are modified by phenoxy of DGEBA, phase dispersion, mechanical properties and rheological properties are significantly improved. The compatibility between phenoxy and MBS is based on thermodynamic miscibility between phenoxy and poly(methyl methacrylate) in MBS. The compatibility between nylon 6 and phenoxy seems to originate from the reactivity between functional groups of the two polymers. The compatibility between DGEBA and MBS is also based on thermodynamic miscibility between the chain component of the epoxy and poly(methyl methacrylate) in MBS. The compatibility between nylon 6 and the epoxy resin originates from reactivity between the functional groups of the two polymers. The role of phenoxy or DGEBA as compatibilizers in nylon 6/MBS blends is demonstrated and the two compatibilizers are compared.

(Keywords: compatibility; nylon; polyhydroxy ether of bisphenol-A)

INTRODUCTION

The use of a compatibilizer is a very common approach in improving the compatibility and properties of incompatible polymer blends. Compatibilizers may be thermodynamically miscible with each polymer component of otherwise incompatible polymer blends and/or may have reactive sites which can result in permanent attractiveness for each polymer component.

One class of thermodynamically miscible compatibilizer is the block copolymer. This type of compatibilizer usually has segments separately miscible with each polymer component of the incompatible polymer pair, acting as a macromolecular surfactant or emulsifying agent[1,2]. For example, poly(styrene-b-methyl methacrylate) copolymer (PS–PMMA) was used as a compatibilizer for the blend of poly(vinylidene fluoride) and Noryl (high impact polystyrene poly-2,6-dimethyl-1,4-phenylene oxide mixture)[3]. The emulsifying effect of PS–PMMA was observed, with significant improvements in phase dispersion, interfacial adhesion and mechanical properties.

Compatibilizers with reactive sites are reactive chemicals or polymers which form crosslinks between components by heat, radiation or peroxide, thus physically tying the components together by way of covalent bonds. Polyamides show poor impact resistance, especially below T_g and in the dry state. Their impact strength may be improved by incorporating a rubber impact modifier, as reported in the literature by several authors[4,5]. This nylon/impact modifier system is a good example of an incompatible system where reactive chemicals are added as compatibilizers.

Nylon/ethylene propylene diene rubbery copolymer (EPDM) blends and nylon/ethylene propylene rubbery copolymer (EPR) blends are examples of nylon/impact modifier systems where a reactive chemical is added as a compatibilizer[6]. A well known compatibilizer of the nylon/EPDM blend is maleic anhydride, which is usually grafted to EPDM and maleic anhydride-grafted EPDM is then blended with the nylon. In this system, the compatibilizing effect originates from the reactivity of maleic anhydride with nylon and with EPDM.

Blends of nylon and the core–shell type impact modifier acrylonitrile–styrene–butadiene (ABS) graft polymers are another example of nylon/impact modifier systems where reactive chemicals are added as compatibilizers. A few compatibilizers of the nylon 6/ABS polymer blend are known. One of them is glycidyl methacrylate (GMA). GMA is grafted to ABS graft polymer and the GMA-grafted ABS is then blended with nylon. Acrylamide, another compatibilizer for the nylon 6/ABS polymer blend, is grafted to nylon and acrylamide-modified nylon is then blended with the ABS polymer[7].

In this work, blends of nylon 6 and another core–shell type impact modifier, methyl methacrylate–styrene–butadiene (MBS) graft polymer Acryloid KM653 (Rohm and Haas), were studied. Nylon 6 is known to be incompatible, or at best poorly compatible, with MBS, and poly(hydroxy ether of bisphenol A) (phenoxy resin) and diglycidyl ether of bisphenol A type epoxy resin (DGEBA) were selected as compatibilizers. Phenoxy was seen as a potential compatibilizer for the system because: (1) phenoxy has been shown to be thermodynamically

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miscible with PMMA, which is a major component of the MBS graft polymer, over the entire composition range[8]; and (2) the epoxy group is known to be very reactive with many functional groups including the amine end-group and the amide group, thus forming covalent bonds with nylons. The repeating unit and end-group of DGEBA are the same as those of phenoxy, but there is a large difference in molecular weight. The epoxy resin is thus expected to show similar behaviour to phenoxy in compatibilizing the nylon 6/MBS system, but the higher population density of epoxy end-groups and the relatively lower quantity of the emulsifying entity (the chain component of the epoxy resin excluding epoxy end-group) in the epoxy resin is expected to lead to some differences in compatibilizing effect as well.

EXPERIMENTAL

The nylon 6 used in this work is a conventional injection-mouldable polycaprolactam obtained from Tongyang Nylon Inc. Two grades with different molecular weight, Toplamid 1011 (medium molecular weight) and Toplamid 1021 (low molecular weight) were used. A core–shell type impact modifier, methyl methacrylate–styrene–butadiene (MBS) graft polymer (Rohm and Haas), was a commercial product designated Acryloid KM653. The poly(hydroxy ether of bisphenol A), obtained from the Union Carbide Corporation, was a commercial product designated Phenoxy PKHH.

Diglycidyl ether of bisphenol A type epoxy resin (DGEBA), obtained from Lucky Corporation, was a commercial product designated LER-7050. The molecular weight of the epoxy resin was 3000–4000.

Nylons were dried in a dehumidifying drier for 24 h and saved in airtight aluminium–polyethylene packages before processing. Blends were prepared by a Leistritz 35 mm twin-screw extruder. Barrel temperature, die temperature, melt temperature and screw rotation speed were set as low as possible. All the extrusion parameters were changed as little as possible from one formulation to another. All the ingredients were tumble-blended and fed through the throat of the extruder.

Blends were examined for morphology and distribution of rubber particles using a transmission electron microscope. All the specimens were prepared by injection moulding and aged in airtight aluminium–polyethylene packages for a week to ensure the same degree of crystallinity and moisture content before mechanical properties were measured according to ASTM procedures.

RESULTS AND DISCUSSION

Morphology

Immiscibility of nylon 6 and MBS. Nylon 6 was extruded with MBS and the distribution of butadiene rubber of MBS was examined using a transmission electron microscope. In *Figure 1*, a TEM micrograph of the nylon 6/MBS blend is presented. The rubber particles are not uniformly distributed in the blend. Agglomerates of rubber particles show poor compatibility between nylon 6 and the shell components of MBS.

Miscibility of MBS and phenoxy. The miscibility between phenoxy and PMMA was verified in previous papers[8,10]. Thus the first step in this study was the examination of miscibility between phenoxy and MBS graft polymer where the shell phase is known to have a substantial amount of polystyrene, which is incompatible with phenoxy, as well as poly(methyl methacrylate). For this purpose, phenoxy was extruded with MBS and the rubber distributions of the blends were examined. All the blends showed uniformly distributed rubber particles. In *Figure 2*, a micrograph of the phenoxy/MBS (80/20) blend is shown. In this micrograph, rubber particles are shown to be uniformly distributed and the continuous phase, a mixture of phenoxy and the shell components of MBS, looks very homogeneous. The uniformity of rubber particle distribution becomes obvious when compared with the micrograph of the simple nylon 6/MBS blend shown in *Figure 1*. From this micrograph, it was concluded that phenoxy and MBS (Acryloid KM653) are thermodynamically miscible or compatible with each other. Alternatively, it can be said that Acryloid KM653 contains enough PMMA in the shell phase to allow miscibility between Acryloid KM653 and phenoxy.

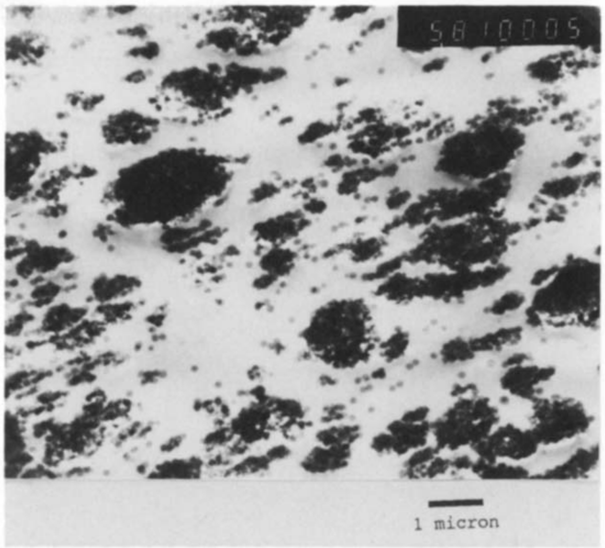

Figure 1 TEM micrograph of the nylon 6/MBS (80/20) blend

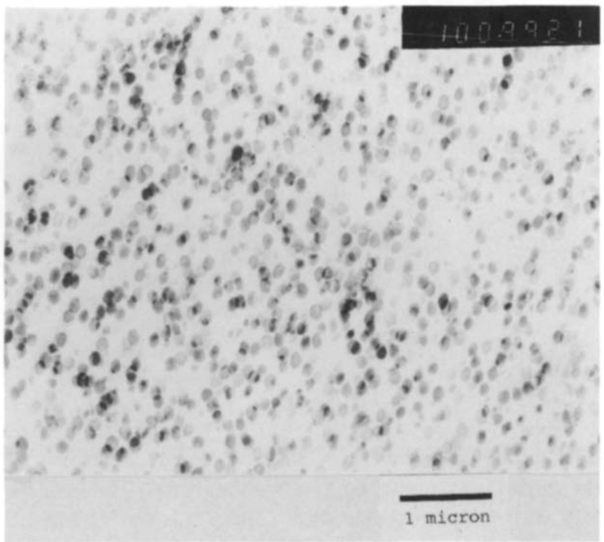

Figure 2 TEM micrograph of the phenoxy/MBS (80/20) blend

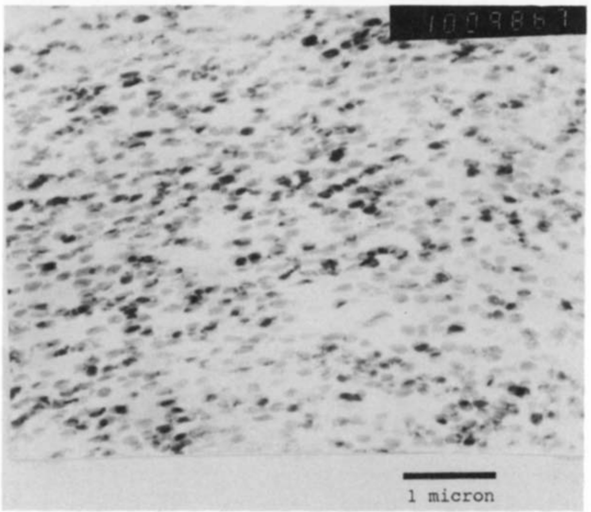

Figure 3 TEM micrograph of nylon 6/MBS/phenoxy (40/20/40) blend

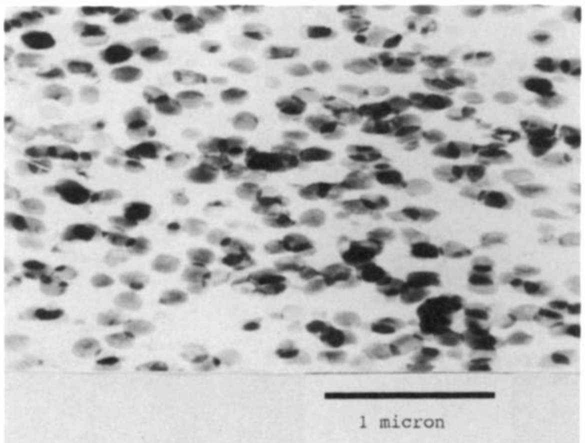

Figure 4 TEM micrograph of nylon/MBS/phenoxy (40/20/40) blend

Evidence from morphology of compatibility or reactivity between nylon 6 and phenoxy. To act as compatibilizer for nylon/MBS blends, phenoxy should be compatible with nylon 6 as well as with MBS. It is well known that epoxy end-groups are reactive with amine end-groups of nylon 6 and other polymers. In this work, the well known reactivity between nylon 6 and phenoxy is demonstrated indirectly by observing the morphology of nylon/phenoxy/MBS blends.

Micrographs of nylon 6/MBS/phenoxy (40/20/40) blends are shown at different magnifications in *Figures 3* and *4*. Rubber particles are uniformly distributed and no agglomerates are seen in these figures.

If there had not been certain compatibility between phenoxy and nylon, phenoxy/MBS, which is in a homogeneous single-phase state, would have been immiscible with nylon, resulting in non-homogeneity of rubber particles in nylon 6/MBS/phenoxy (40/20/40) blends. Such blends, however, showed a good distribution of rubber particles, so it can be said that the nylon/phenoxy mixture is homogeneous and there exists some kind of compatibility between nylon 6 and phenoxy. From this morphology and the suggestion in the literature of reactivity between epoxy and amine groups, it is postulated that covalent bonds form between nylon 6 end-groups and the epoxy end-groups of phenoxy. Thus the nylon 6/MBS/phenoxy system can be rewritten as the phenoxy-grafted(modified) nylon 6/MBS system, and phenoxy-modified nylon 6 may be considered to be thermodynamically miscible with MBS.

Level of homogeneity of nylon/phenoxy blend. Any multicomponent polymeric system can be said to be either in the single-phase or the multiphase state depending on the level of observation.

A binary nylon 6/phenoxy (40/40) blend can be considered to be half phenoxy and half nylon 6 block copolymer, i.e. phenoxy-modified nylon. This block copolymer can also be said to be either macroscopically single-phase or multiphase at a certain microscopic level. This level of homogeneity is of interest to future work. However, at this point, two facts, the thermodynamic miscibility between phenoxy and MBS, and the uniformity of rubbers in the nylon 6/MBS/phenoxy (40/20/40) blend, indicate that the phenoxy/nylon 6 (40/40) diblock copolymer forms a single phase at the level of the dimensions of the rubber particle. Phenoxy might have formed dispersed phase in the nylon 6 phase (or nylon 6 might have formed dispersed phases in the phenoxy phase) but the domain size of the phenoxy phase must be smaller than the order of the rubber particle size, as the rubber distribution is uniform in the blend.

Effect of phenoxy content on nylon/phenoxy/MBS blend morphology. The role of phenoxy as compatibilizer for nylon/MBS systems is now clear from the morphological standpoint. It means that the addition of any amount of phenoxy to the nylon/MBS system will increase compatibility. However, the phenoxy content (40%) in the nylon 6/MBS/phenoxy (40/20/40) blend is somewhat too large and was therefore decreased. In *Figure 5*, a micrograph of nylon 6/MBS/phenoxy (80/20/5) blend is shown. In this formulation rubber particles are not as well distributed as in the nylon 6 blend discussed above. However, the uniformity of rubber particles in this formulation looks somewhat better than in the simple nylon 6/MBS blend shown in *Figure 1*. This relatively poor distribution of rubber can be explained as follows. The nylon 6/MBS/phenoxy (80/20/5) system can be recast

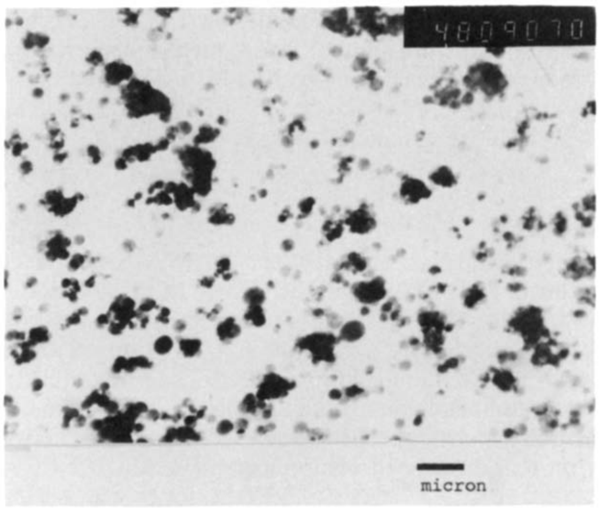

Figure 5 TEM micrograph of nylon 6/MBS/phenoxy (80/20/5) blend

as a phenoxy (5)-grafted-nylon 6 (80)/MBS system. In this system, a smaller quantity, only 5 parts, of phenoxy is grafted to 80 parts of nylon 6 and the total quantity of the phenoxy phase is smaller (i.e. only 5 out of 80 parts of nylon are modified by phenoxy). Phenoxy-grafted nylon 6 (5/80) (a mixture of phenoxy-grafted nylon 6 diblock copolymer and pure nylon 6) thus is not powerful enough in terms of thermodynamic miscibility to disperse MBS rubber particles uniformly. Therefore rubbers are not well dispersed in a phenoxy-grafted (modified) nylon 6 (5/80).

In nylon 6/MBS/phenoxy blends, uniformity of rubber particles or morphological compatibility of the whole system change depending on the relative quantity of each component.

Morphology of nylon/MBS/DGEBA systems. Nylon 6/MBS/DGEBA (80/20/*x*) blends were extrusion compounded at 260°C and morphology was examined using transmission electron microscopy (TEM). A TEM micrograph of a nylon 6/MBS/DGEBA (80/20/1) blend is presented in *Figure 6*. In this blend, uniformity of the butadiene rubber particles of MBS was not much better than in the nylon 6/MBS (80/20) blend shown in *Figure 1*. Agglomerates of rubber particles show poor distribution of MBS in the nylon 6 matrix. The role of DGEBA as a compatibilizer for the system is not very obvious from this morphological observation.

Evidence of compatibility from rheological behaviour

Effect of phenoxy on processability. The rheological effect of phenoxy content is studied by measuring the melt flow index (ASTM D1238 at 250°C, 2160 g) and results are shown in *Table 1*. The melt flow index increased from 3 g/10 min for simple nylon 6/MBS (80/20) to 12 g/10 min with the addition of 5 parts phenoxy per hundred parts of the blend and levelled off with a further increase up to 7.5 parts. The increase of melt flow index can be explained by the elimination of interfacial tension between nylon 6 and MBS. The polymeric compatibilizer phenoxy behaved as a macromolecular surfactant.

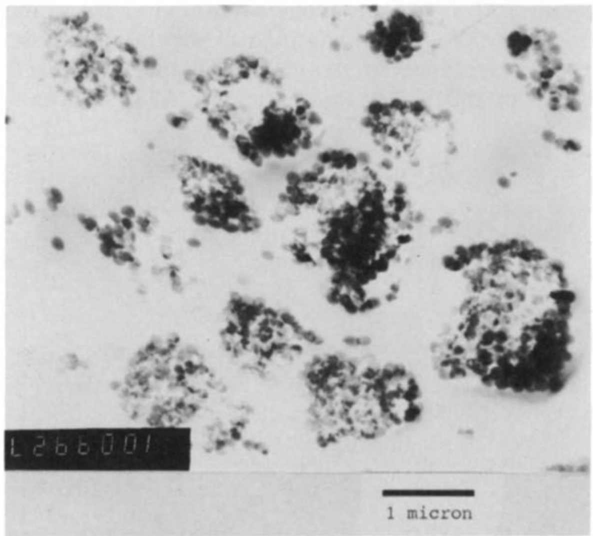

Figure 6 TEM micrograph of nylon 6/MBS/DGEBA (80/20/1) blend

Table 1 Effect of phenoxy content on melt flow index (ASTM D1238 at 250°C and 2160 g)

Composition (nylon 6/MBS/phenoxy)	Melt flow index (g/10 min)
80/20/0	3
80/20/5	12
80/20/7.5	12
80/20/10	10

Table 2 Effect of DGEBA content on melt flow index (ASTM D1238 at 260°C and 2160 g)

Composition (nylon 6/MBS/DGEBA)	Melt flow index (g/10 min)
80/20/0	3
80/20/1	6
80/20/2	4
80/20/5	3.5

Increases in molecular weight or crosslinks are known to lower processability or flowability. Most core–shell type impact modifiers lower processability as in the case of ABS in ABS/nylon blends. In the case of the nylon 6/MBS/phenoxy blend in this study, nylon 6 is not chemically bound to MBS, nor is there a permanent crosslink between nylon 6 and MBS. Instead, polymeric compatibilizer-modified nylon 6 (phenoxy-modified nylon 6) is thermodynamically blended to the shell phase of MBS. Forces between the molecule chains of poly(methyl methacrylate) and phenoxy are the van der Waals force and/or the hydrogen bond[9,10]. Unlike covalent bonds, these forces always become weak or disappear at the polymer processing temperatures, imparting fluidity. This is the explanation for the good processability of the nylon 6/MBS/phenoxy blend, confirmed by the melt flow index measurements of *Table 1*. This, from a commercial point of view, is a very important and advantageous characteristic of the nylon 6/MBS/phenoxy blend compared with other nylon 6/impact modifier systems where covalent bonds tie the components together, giving poor processability. Good processability differentiates the nylon 6/MBS/phenoxy blend from other crosslink-based nylon 6/impact modifier blends. Notice, however, that the melt flow index decreased somewhat with the addition of 10 parts of phenoxy.

Effect of DGEBA on flow properties. In *Table 2*, the melt flow index (ASTM D1238) is shown for the nylon 6/MBS/DGEBA blends with different DGEBA contents. With the addition of 1 part DGEBA to nylon 6/MBS (80/20), the processability of the blend did increase, as in the case with the nylon 6/MBS/phenoxy (80/20/5) blend. However, with further addition of DGEBA, the processability decreased. This decrease was also observed in the nylon 6/MBS/phenoxy (80/20/10) blend. With these high concentrations of DGEBA, there seem to be an excessive number of epoxy end-groups of DGEBA, forming more than the necessary number of covalent bonds between nylon 6 and DGEBA. These excessive covalent bonds, rather than contributing to the compatibilizing effect between nylon 6 and DGEBA, decreased the flowability.

Decrease in melt flow index with increase in DGEBA (from 2 to 5 parts) is an indication that covalent bonds form between the functional groups of DGEBA and nylon, which is a cause of the compatibility between nylon 6 and DGEBA.

For the nylon 6/MBS/DGEBA (80/20/1), the effect of compounding processing temperature on melt flow index

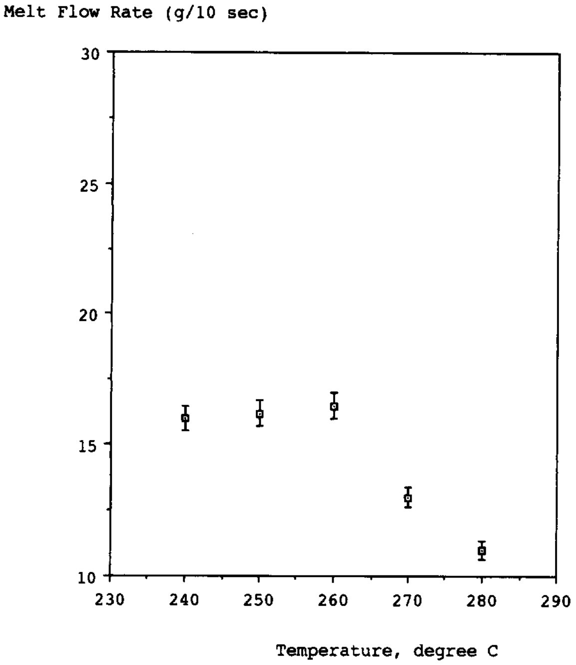

Figure 7 Effect of processing temperature on melt flow index for nylon 6/MBS/DGEBA (80/20/1) blends

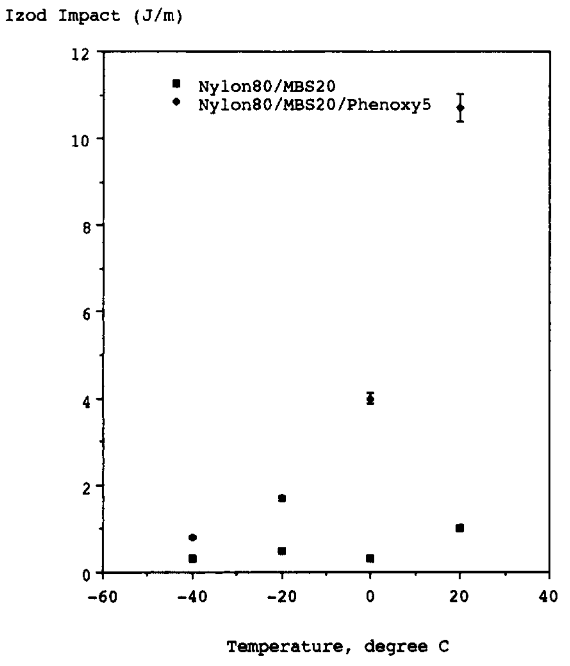

Figure 8 Notched Izod impact strength for nylon 6/MBS/phenoxy (80/20/5) blend and nylon 6/MBS (80/20) blend at different temperatures

is shown in *Figure 7*. Melt flow index decreased from 17 g/10 min for a blend compounded at 240°C to 12 g/10 min compounded at 280°C. Decrease in melt flow index with increase in processing temperature is another indication that covalent bonds form between the functional groups of DGEBA and nylon during extrusion blending. Melt flow index decreased as the number of covalent bonds formed between component molecular chains, which do not disappear with increase in temperature during melt index measurement, or in secondary processing steps such as injection moulding and blow moulding, increased with reaction temperature according to the Arrhenius equation.

Mechanical properties and evidence of compatibility

Mechanical properties of nylon 6/MBS/phenoxy. In *Figure 8*, notched Izod impact strength of the nylon 6/MBS/phenoxy (80/20/5) blend is shown to be much higher than that of the simple nylon 6/MBS (80/20) blend at all temperatures measured. In *Figure 9*, notched Izod impact strength at room temperature for nylon 6/MBS/phenoxy (80/20/x) blend with different values of x up to 10 is shown. Notched Izod impact strength increased with increase in phenoxy content very fast up to 4–6 parts but levelled off with further increases. From the viewpoint of notched Izod impact strength, 4–6 parts is a sufficient quantity of phenoxy as compatibilizer. The role of phenoxy as a compatibilizer in the nylon 6/MBS (80/20) blend is clearly shown by this mechanical property measurement, while the role was less obvious in the morphological observations on *Figures 1* and *5*.

Drop weight impact resistance was measured with a mass of 3.765 kg and a velocity of 584.2 cm s^{-1}. In *Figure 10a* and *b*, results are presented for the nylon 6/MBS (80/20) blend (*Figure 10a*) and nylon 6/MBS/phenoxy (80/20/5) blend (*Figure 10b*). The energy absorption at the final fracture point for nylon 6/MBS (80/20) blend is 40 J. When 5 parts of phenoxy were added, the energy absorption at the final fracture point increased to 44 J. The force curve of nylon 6/MBS/phenoxy (80/20/5) (*Figure 10b*) exhibits a shoulder during the later stage of rupture, which is characteristic of rubber-modified resins. In contrast, a shoulder is not observed on the nylon 6/MBS (80/20) force curve (*Figure 10a*). The implication here is that, without compatibilizer, rubber particles in MBS do not act as impact modifier. Time to final point of fracture also increased with addition of phenoxy. These drop weight impact resistance increases were reproducible with other levels of phenoxy content.

Figures 11, *12*, *13* and *14* show tensile strength, ultimate elongation, flexural strength and flexural modulus at room temperature for nylon 6/MBS/phenoxy (80/20/x) blends with different phenoxy contents. All the mechanical

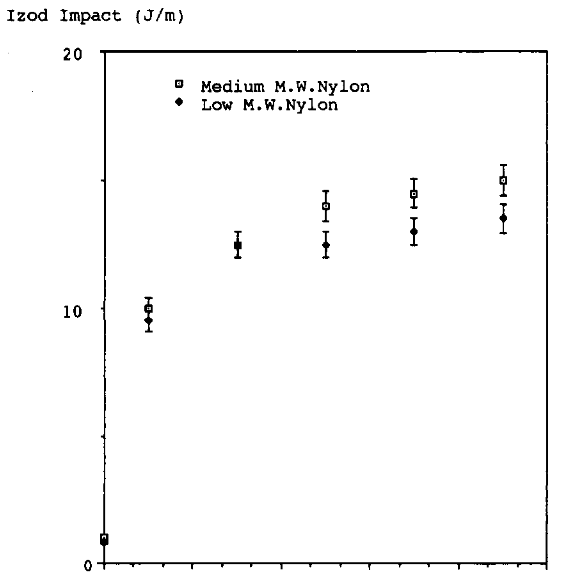

Figure 9 Notched Izod impact strength at room temperature for nylon 6/MBS/phenoxy (80/20/x) blends for several values of $x \leqslant 10$ and nylon 6 of two different molecular weights

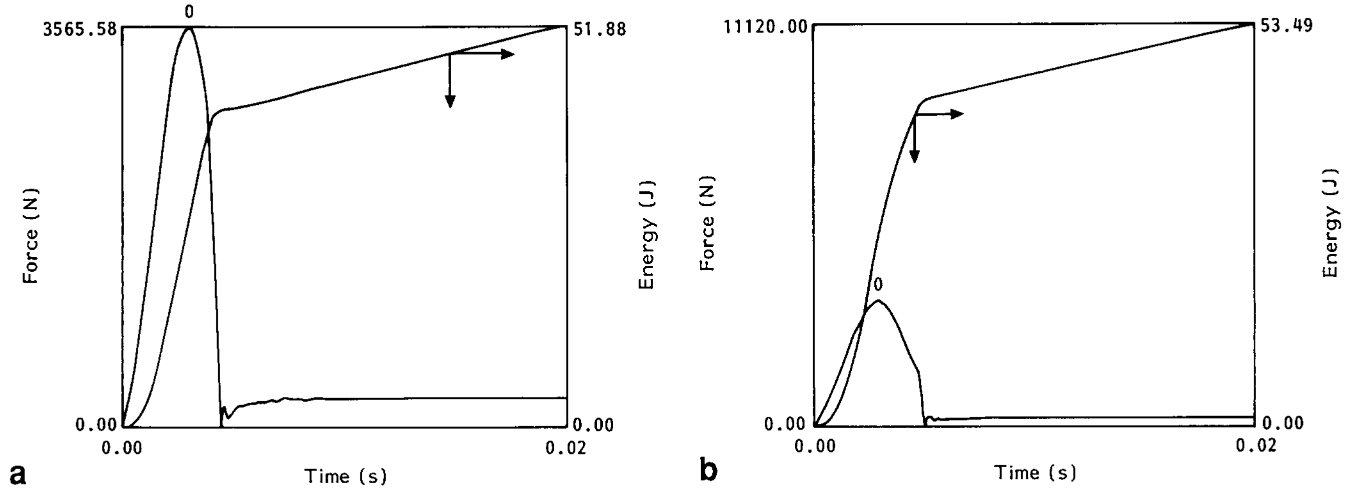

Figure 10 Drop weight impact resistance for (a) nylon 6/MBS (80/20) blend and (b) nylon 6/MBS/phenoxy (80/20/5) blend

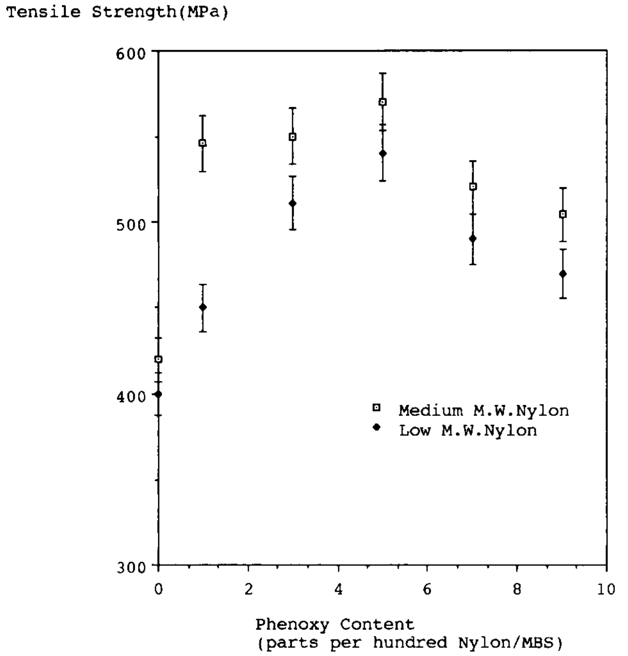

Figure 11 Tensile strength (crosshead speed 10 mm min^{-1}) at room temperature for nylon 6/MBS/phenoxy (80/20/x) blends with different phenoxy contents and nylon 6 of two different molecular weights

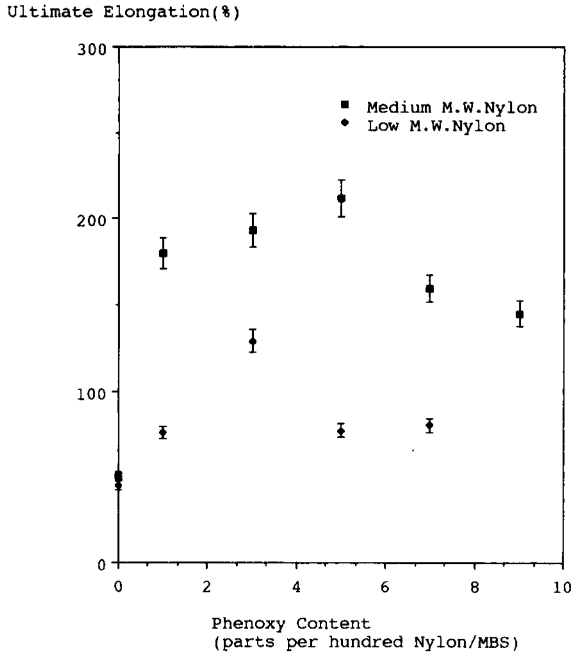

Figure 12 Ultimate elongation (crosshead speed 10 mm min^{-1}) at room temperature for nylon 6/MBS/phenoxy (80/20/x) blend with different phenoxy contents and nylon 6 of two different molecular weights

properties increased with addition of any quantity of phenoxy, but were maximized at phenoxy contents of 4–6 parts per hundred (pph). Tensile strength, ultimate elongation, flexural strength and flexural modulus all increased with increase in phenoxy up to 4–6 pph nylon 6/MBS (80/20) and decreased with further increase in phenoxy. Above 4–6 pph nylon 6/MBS (80/20), phenoxy starts to act as a third component and contribute its own properties to the blend properties by the additive rule, while continuing to behave as a compatibilizer. Thus these mechanical property behaviours should be explained by regarding phenoxy as simultaneously a compatibilizer and a third component. These mechanical property results show that there exists some kind of compatibility between nylon 6 and phenoxy. Our preliminary Fourier transform infra-red study shows the disappearance of the epoxy group when nylon 6 was blended with phenoxy. More studies are required to support this conclusion.

Table 3 Effect of DGEBA on notched Izod impact strength (sample thickness 0.635 cm) at room temperature

Composition (nylon 6/MBS/DGEBA)	Notched Izod impact strength (J cm^{-1})
80/20/0[a]	6
80/20/1[b]	20
80/20/2	19
80/20/5	19

[a] Shown in *Figure 1*
[b] Shown in *Figure 6*

Mechanical properties of nylon/DGEBA/MBS. Notched Izod impact strength for the nylon 6/MBS (80/20) blend and nylon 6/MBS/DGEBA (80/20/x) blends with different DGEBA content extruded at 260°C are shown in *Table 3*. Impact strength increased with addition of 1 part

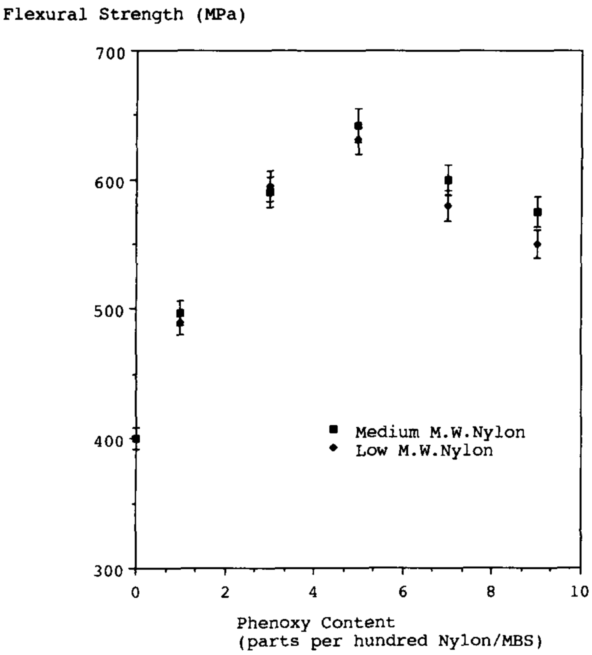

Figure 13 Flexural strength at room temperature for nylon 6/MBS/phenoxy (80/20/x) blends with different phenoxy contents and nylon 6 of two different molecular weights

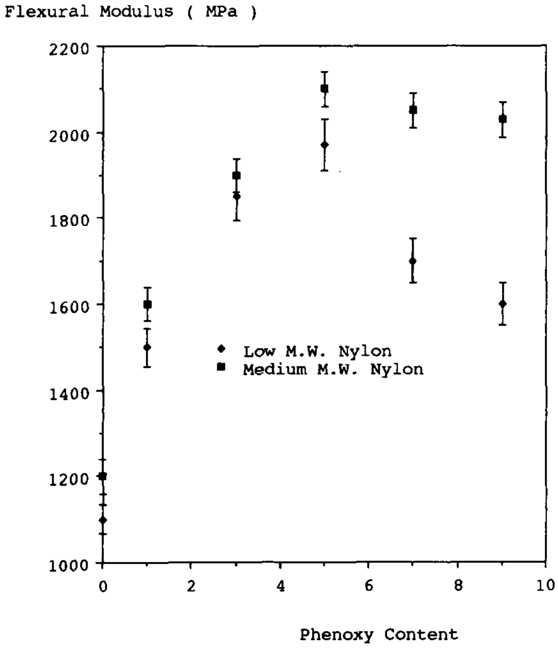

Figure 14 Flexural modulus at room temperature for nylon 6/MBS/phenoxy (80/20/x) blend with different phenoxy contents and nylon 6 of two different molecular weights

DGEBA per hundred nylon 6/MBS (80/20) and further increases in the amount of epoxy resin did not increase the impact strength.

Drop weight impact resistance force and energy curves for nylon 6/MBS/DGEBA (80/20/1) (*Figure 15*), and nylon 6/MBS/DGEBA (80/20/5) (*Figure 16*) are presented and compared with the simple nylon 6/MBS (80/20) blend shown in *Figure 10a*. In *Figure 10a*, the energy absorption at final fracture point for the nylon 6/MBS blend is shown to be 40 J. With the addition of 1 part of DGEBA, energy absorption at final fracture point increased to 51 J. When 5 parts DGEBA were added, energy absorption at the final fracture point was 50 J. Force curves of nylon 6/MBS/DGEBA (80/20/x) (*Figures 15* and *16*) also have shoulders during the later stage of rupture, which is characteristic of rubber-modified resins. Time to final point of fracture also increased with addition of DGEBA.

Impact modification requires reasonable force, i.e. compatibility, between the impact modifier and matrix polymer components in the solid state. MBS did not act as an impact modifier until DGEBA was added. Thus DGEBA is also considered to act as compatibilizer, increasing the interchain force between nylon 6 and MBS. In the cases of both nylon 6/MBS/phenoxy and nylon 6/MBS/DGEBA, interchain forces between matrix polymer and impact modifiers can be increased and impact modification can be achieved without much improvement of the uniformity of impact modifier distribution.

Dependence of mechanical properties of nylon 6/DGEBA/MBS on blending temperature. Nylon 6/MBS/DGEBA (80/20/1) blends were compounded at different temperatures and mechanical properties were measured. The effect of compounding temperature on properties (notched Izod impact strength, ultimate elongation, tensile strength and flexural strength/modulus of the blends) in the solid state are shown in *Figures 17–20*. Notched Izod impact strength increased very substantially with processing tem-

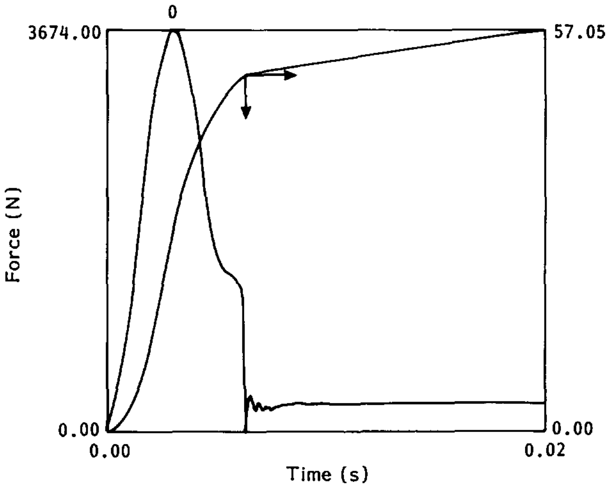

Figure 15 Drop weight impact resistance force (a) and energy (b) curves for nylon 6/MBS/DGEBA (80/20/1) blend

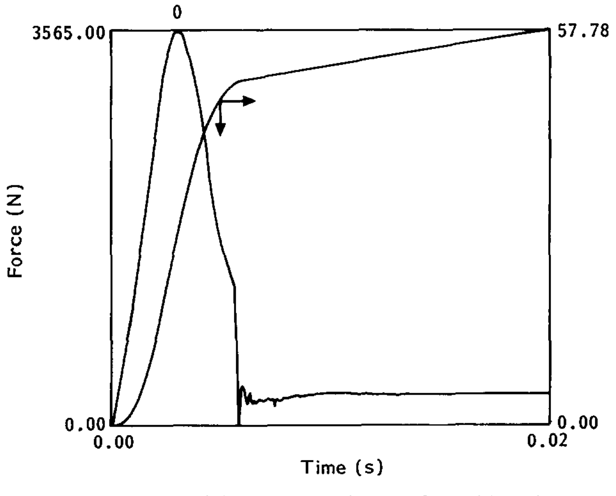

Figure 16 Drop weight impact resistance force (a) and energy (b) curves for nylon 6/MBS/DGEBA (80/20/5) blend

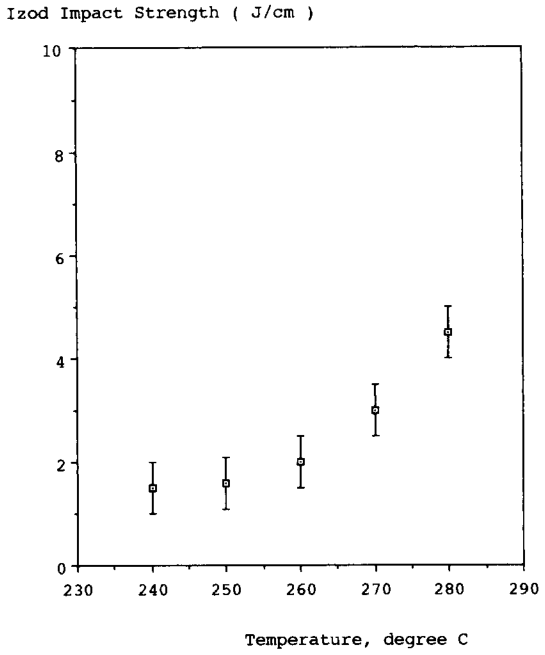

Figure 17 Effect of processing temperature on notched Izod impact strength for nylon 6/MBS/DGEBA (80/20/1) blends

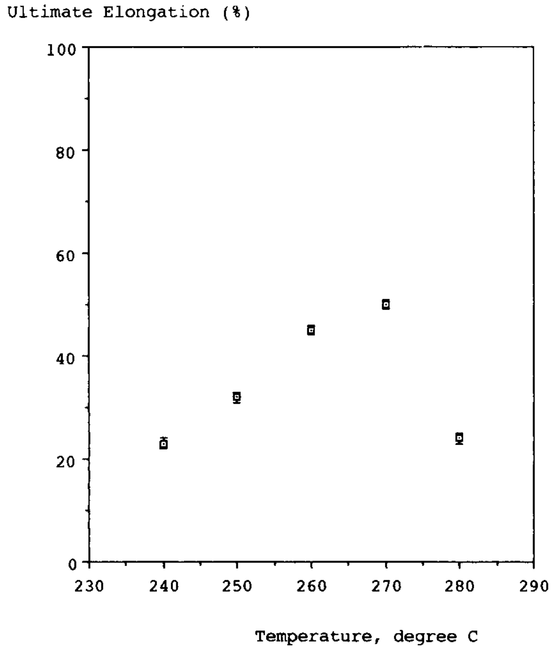

Figure 18 Effect of processing temperature on ultimate elongation for nylon 6/MBS/DGEBA (80/20/1) blends

perature. Ultimate elongation also increased with processing temperature but dropped above 280°C. Flexural strength and flexural modulus are shown in *Figure 20* to decrease with processing temperature.

The changes in solid-state properties of nylon 6/MBS/DGEBA blends with processing temperature can give additional clues on the origin of compatibility. Increase in impact strength means increase in intermolecular forces between components in the solid state. Among many intermolecular forces, the van der Waals force, hydrogen bonds and crosslink formation are considered to be the main forces for compatibility between polymers in the polymer blend.

First, let us consider the van der Waals force and hydrogen bond of thermodynamically miscible systems. The numbers of van der Waals forces or hydrogen bonds between two miscible components in the blend do not depend on the processing temperature as long as the compounding temperature and shear rate are high enough. The compounding processing temperature does not affect the number of these forces. However, the strength of each hydrogen bond and van der Waals force may change with temperature. Forces based on van der Waals forces and hydrogen bonds are a function only of the temperature of the material and are not influenced by processing temperature or temperature history. For example, in the case of thermodynamically miscible systems such as PPE/HIPS, poly(vinyl chloride)/MBS,

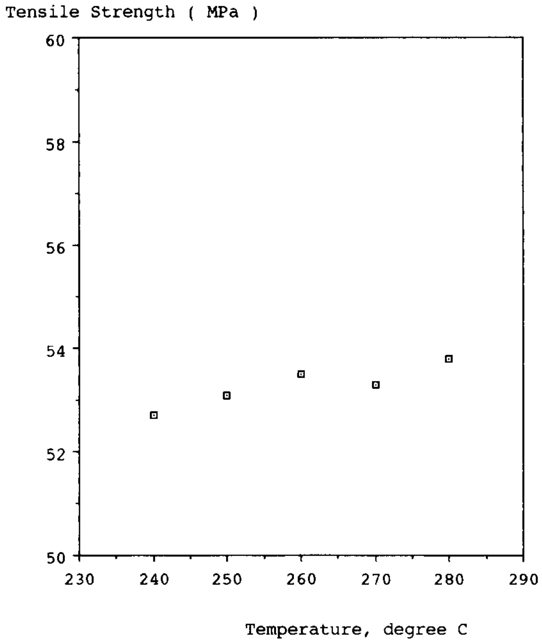

Figure 19 Effect of processing temperature on tensile strength for nylon 6/MBS/DGEBA (80/20/1) blends

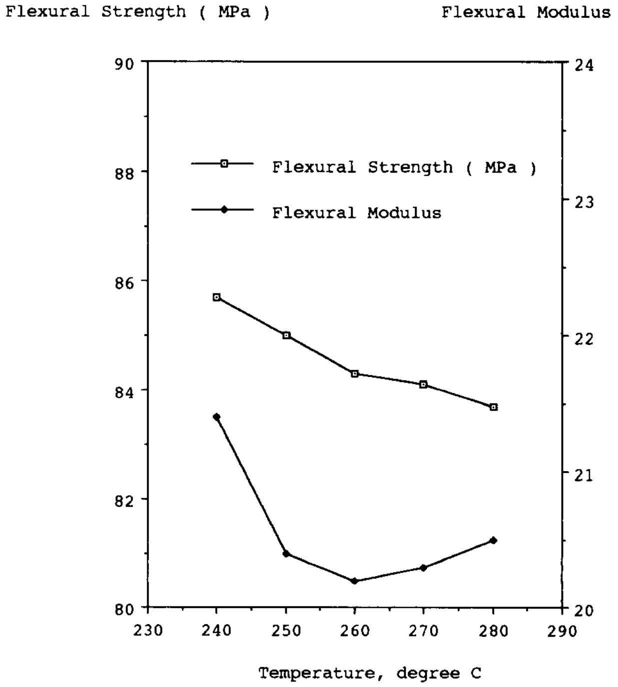

Figure 20 Effect of processing temperature on (a) flexural strength and (b) flexural modulus for nylon 6/MBS/DGEBA (80/20/1) blends

or phenoxy/PMMA, different compounding processing temperatures do not generally change the physical properties in the solid state. This is because interchain forces in the solid state depend on the temperature of the measurement, and not on the processing temperature (temperature history).

Chemical reactivity or the number of covalent bonds formed through chemical reaction is, however, a function of the compounding processing temperature. According to the Arrhenius equation, the higher the reaction temperature, the higher the reactivity. Moreover, covalent bonds formed at the reaction temperature continue to exist from the high processing temperature to the low solid-state temperature. Thus, in systems where chemical reaction forms covalent bonds between polymers, the solid-state properties are dependent on the temperature history. In other words, in the covalent bond-forming blend systems, the solid state 'remembers' the processing temperature history. Of the van der Waals force, hydrogen bond and covalent bond (a reaction between two functional groups), only the last is dependent on temperature history (here the processing temperature).

For the nylon 6/MBS/DGEBA system, the solid-state properties were dependent on temperature history. Thus, the intermolecular forces must originate from covalent bonds between polymers, formed by the reaction between the functional groups of DGEBA and nylon. This increase in intermolecular forces (compatibility) with temperature for the system is explained by the higher number of covalent bonds, and therefore higher forces, between components per unit volume.

Ultimate elongation increased with temperature but dropped at 280°C. This drop seems to originate from degradation of the polymers. At this temperature the extrudate indeed became yellow, which indicates oxidation and probably degradation.

Comparison between phenoxy and DGEBA

As shown in *Table 3*, notched Izod impact strength at room temperature for nylon 6/MBS (80/20) increased suddenly when 1 part DGEBA was added but levelled off with further increase in DGEBA. Comparison of *Figures 10a*, *14* and *15* also shows that drop weight impact strength at room temperature for nylon 6/MBS (80/20) increased when 1 part DGEBA was added but levelled off with further increases. Thus, with respect to these impact strengths, about 1 part of DGEBA as compatibilizer is sufficient. This is consistent, from the viewpoint of normality of epoxy end-groups, with the optimum quantity of phenoxy content (5 parts) for the nylon 6/MBS/phenoxy (80/20/*x*) blend, as the molecular weight of phenoxy is approximately 20 000 and that of DGEBA is about 3000–4000, and therefore the end-group population is five times greater for DGEBA than for phenoxy. This also indicates that the epoxy end-group, and not the hydroxyl group, of epoxy resins plays the major role in covalent bond formation with nylon 6.

In the case of the nylon 6/MBS/phenoxy (80/20/5) blend, it was shown that nylon 6 was not chemically bound to MBS, and there was no permanent crosslink between nylon 6 and MBS. Instead, polymeric compatibilizer-modified nylon 6 (phenoxy-modified nylon 6) was thermodynamically blended with the shell phase of MBS. Forces between molecule chains of poly(methyl methacrylate) and phenoxy were considered to be van der Waals forces or hydrogen bonds[10]. In the nylon 6/MBS/DGEBA (80/20/1) system, the epoxy group population density is similar to that in the nylon 6/MBS/phenoxy (80/20/5) but the DGEBA chain is shorter than the phenoxy chain. Thus less emulsifying entity (the chain component of DGEBA excluding the epoxy end-group) acts as compatibilizer between DGEBA-modified nylon 6 and the shell phase of MBS. For a given population density of epoxy end-group, DGEBA-modified nylon 6 and the MBS pair have a weaker thermodynamic miscibility (less compatibilizing effect) than the phenoxy-modified nylon 6 and MBS pair. This weak thermodynamic miscibility may explain the relatively poor distribution of MBS in the nylon 6/MBS/DGEBA system. To increase the level of the emulsifying entity of the nylon 6/MBS/DGEBA (80/20/*x*) to that in the nylon 6/MBS/phenoxy (80/20/5) mixture, more DGEBA should be added, but this would also increase the epoxy end-group population density. However, it can be seen in *Figures 18*, *19* and *20* that blends of nylon 6/MBS/DGEBA (80/20/1) extruded at 260°C have not consumed all the epoxy end-groups, thus even 1 part of DGEBA seems to be in excess for the system. As the DGEBA content is raised to increase the emulsifying entity, the number of crosslinks will increase and the flowability will decrease.

Other materials

The polyamide studied in this work was polycaprolactam (nylon 6). As the compatibility between nylon 6 and epoxy resins originates from the reactivity between functional groups of the two polymers, other polyamides, such as poly(hexamethylene adipamide) (nylon 6,6) and poly(hexamethylene sebacamide) (nylon 6,10), may be substituted for nylon 6 with similar results, as long as end-groups are the same.

Advantages of these systems

When impact modifiers form substantial numbers of covalent bonds with nylon 6, problems of poor processability may be encountered. Many of the above-mentioned modified core–shell type impact modifier ABS/nylon systems showed poor processability, whereas in the nylon 6/MBS/phenoxy system, processability is excellent, reaching an acceptable level with a reasonable amount of DGEBA, around 1 pph nylon 6/MBS.

In thermodynamically miscible systems which do not involve covalent bonds between component polymers, blends with any ratio of two components within the window of miscibility are possible, giving a wider choice of properties. For example, polystyrene/poly-2,6-dimethyl-1,4-phenylene oxide is a thermodynamically miscible system, and blends with any ratio of the two components are possible. The nylon 6/MBS/phenoxy system can be rewritten as the phenoxy-modified nylon 6/MBS system; phenoxy-modified nylon 6 is thermodynamically miscible with MBS and thus blends with any ratio of the two components are possible. This is considered to be an advantage over other nylon 6/impact modifier systems where compatibility relies only on covalent bond formation.

The nylon 6/MBS/DGEBA system can similarly be rewritten as the DGEBA-modified nylon 6/MBS system and since DGEBA-modified nylon 6 is thermodynamically miscible with MBS, blends with any ratio of the two components are possible. In this case, however, the emulsifying entity is relatively small and the compounding requires a more intensive shear rate.

Characteristics of the systems

The compatibility of nylon 6/MBS/DGEBA or nylon 6/MBS/phenoxy is based on covalent bond formation as well as thermodynamic miscibility. In purely thermodynamically miscible systems not involving covalent bond formation, such as PPE/HIPS and PVC/MBS, two components mix at the molecular level resulting in a homogeneous phase with uniform rubber distribution. When chemical reactivity is involved to increase compatibility, two heterogeneous phases may exist and covalent bonds may occur at the boundary of two phases. In this case, impact modifiers may or may not be distributed uniformly. It was shown in this work that impact modification of certain systems may be improved (or interphase force may be increased) without perfect uniformity of rubber particle distribution.

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