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Thermal behaviour of nylon 6-poly(ether–esteramide) block copolymers

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Block copolymers have been produced by anionic polymerization of caprolactam with end-functionalized soft-block components derived from polymeric polyols. This method of synthesis gives rise to linear segmented block copolymers with alternating polyether soft blocks and polyamide hard blocks. Copolymers with 10–50% w/w of polyether polyol prepolymer have been the particular focus of attention in this work because of their better physical integrity than copolymers of other compositions. Their phase inversion and morphology/property relationships have been examined by means of differential thermal calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). In this work, the polymers have been hand-cast, but the materials do find application in the reaction injection moulding field.

1. Introduction

Reaction injection moulding (RIM) was rapidly developed in the early seventies to produce vehicle parts that would meet US legislation on the impact requirements for automobiles. The RIM processes at that time were based largely on polyurethane materials. The success of polyurethane-based RIM methods led to a search for other chemical systems which were suitable for the process without major modifications of the available equipment. Lactams, epoxies, polyesters and others were shown to have potential for the RIM process. The polymerization of caprolactam-based polymers have received particular interest as a commercial non-urethane RIM process because of its relatively low cost and reasonably fast reaction rates, as well as the good mechanical performance of the polymers.

In 1981, Hedrick and Gabbert reported a new nylon 6 block copolymer system (NBC) for RIM which was based on the anionic polymerization of caprolactam with end-functionalized soft-block components derived from polyether polyols [1–3]. This system became a commercial process in 1982. Nylon 6 block copolymers have the structure of alternating polyether soft blocks and polyamide hard blocks. The soft block contributes high toughness, elongation and flexibility, whereas the hard block contributes high strength, rigidity, chemical resistance and high melting temperature of the polymer. By varying the composition of caprolactam and the poly(ether–esteramide) prepolymer in the reaction mixture, it is possible to produce a variety of block copolymers with a wide range of morphologies and properties. These copolymers have found use as high temperature engineering materials, their performance being enhanced by the incorporation of fibrous reinforcements [2, 4], but little has been reported on the precise impact of copolymer composition and thermal history of the materials which can have a significant impact on observed properties.

2. Materials

Caprolactam, poly(ether–esteramide) prepolymer and the catalyst (caprolactam magnesium bromide), the three main reagents for preparing NBC, were stored in a desiccator because moisture could render the catalyst inactive. These reagents were supplied by DSM, The Netherlands.

3. Experimental procedure

3.1. Preparation of NBC

3.1.1. Virgin materials

The reaction mixture, which contained caprolactam, the prepolymer and the catalyst, was divided into two parts in a weight ratio of approximately 1:1. They were placed into two vessels which were then heated separately. Vessel A, which contained the prepolymer and a part of the total amount of caprolactam was heated to 90 °C. This temperature was maintained until all the caprolactam had melted. The remaining caprolactam, which was in vessel B, was heated to 110 °C. The catalyst was then poured into the vessel. The temperature was maintained until all the catalyst was well dissolved into the caprolactam. The temperature was then lowered to ca. 90 °C. The contents of vessels A and B were thoroughly mixed together and immediately poured into a mould which had been preheated in an oven at 140 °C. Polymerization was allowed to continue for 5 min before the solid product was removed from the mould. Block copolymers containing 10, 20, 30, 40 and 50% w/w of prepolymer were prepared with a constant catalyst concentration of

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10% w/w for all formulations (Mooij [5] suggested that a typical NYRIM formulation could contain 10–40% of polyether soft block). These copolymers were regarded as "virgin" materials. No problems were encountered with the "killing" of active initiating or propagating species by reaction with atmospheric moisture during reaction.

3.1.2. Annealed materials

Annealed NBC samples were prepared from the corresponding "virgin" materials (section 3.1.1). A common thermal history was imposed upon all the samples; they were first heated to 190 °C in a N_2 atmosphere and maintained at this temperature for 30 min before being quenched in liquid nitrogen. Finally, they were annealed at 135 °C for 17 h in a N_2 atmosphere.

3.2. Differential scanning calorimetry (DSC)

The morphologies of the "virgin" and annealed NBC samples were examined by means of a differential scanning calorimeter (Perkin-Elmer DSC 7). A heating–quenching–reheating programme was used to impose a common thermal history upon all the virgin samples as follows: each sample was heated from 0 to 237 °C at a rate of 20 °C min^{-1}, and maintained at this temperature for 5 min before quenching to 0 °C at a rate of 200 °C min^{-1}. The sample was then kept at 0 °C for 5 min. Finally, the sample was reheated to 237 °C at a rate of 20 °C min^{-1}, and a thermal trace was recorded. The quenching and reheating processes were not applied to the previously annealed samples (Section 3.1.2). These materials were simply subjected to a thermal scan in the DSC from 0 to 237 °C.

3.3. Dynamic mechanical thermal analysis (DMTA)

The temperature-dependent viscoelastic properties of NBC were studied using a dynamic mechanical thermal analyser (PL Thermal Sciences DMTA MK II). Samples (virgin and annealed) of ca. 8 mm wide, 30 mm long and 3 mm thick were prepared. All the samples were tested using the dual-cantilever bending mode. The mounted sample was enclosed in a temperature-controlled chamber. The operating temperature range for the virgin materials was from − 90 to 100 °C, whilst the one for the annealed materials was from − 90 °C to ca. 230 °C, depending on the melting point of the sample. The heating rate was 2 °C min^{-1} and the operating frequency was 1 Hz. The storage modulus, loss modulus and mechanical damping factor for each sample were automatically recorded by computer throughout the test.

4. Results and discussion

4.1. Differential scanning calorimetry (DSC)

The technique of DSC was adopted to study the basic morphologies and crystallization phenomena of NBC ecause of the enthalpic changes which occur for the processes of interest in this work. A pre-set heating–quenching–reheating programme was required in the work in order to impose a common thermal history upon all the samples (section 3.2). When analysing a thermoplastic polymer by DSC the thermal history effect makes it difficult to make any definite conclusions about the material from a single thermogram. This becomes more complicated when comparing different materials or dealing with multi-component systems such as NBC. When a crystallizable polymer is melted and then allowed to cool slowly, the polymer chains may have enough time to orientate themselves to form crystals. However, an amorphous material may result from fast cooling because the molecules are frozen into a disordered network. Without a common thermal history, therefore, it is inappropriate to compare the morphologies of the block copolymers.

The thermograms of virgin samples obtained after the heating–quenching–reheating programme are shown in Fig. 1. It can be seen that all the materials have melting temperatures at ca. 207–218 °C. The double melting peaks for the 10% material (a major peak and a shoulder for the 20% material) suggest that there are different nylon 6 crystal structures in the material. Kurz [6] has also observed multiple melting peaks using DSC.

It has been reported in our previous work [7] that NBC contain incompatible amorphous soft blocks and crystallizable hard blocks, and it was suggested that the disperse/continuous phase inversion takes place at compositions containing 20–30% w/w polyether prepolymer. It is expected that when soft blocks form the continuous phase, the material is likely to acquire an amorphous structure after quenching because the inner polyamide disperse domains are refrained from crystallization from the melt. Nevertheless, upon reheating through the glassy region, the molecular mobility will increase and the hard blocks are then able to "cold crystallize" [8], as demonstrated by the exothermic peaks at temperatures of ca. 69–86 °C for the 30, 40 and 50% materials (Fig. 1). However, these exothermic peaks are not seen for the 10 and 20% materials, indicating different morphologies (better ordered structures) from the amorphous counterparts. The absence of cold crystallization peaks in these samples suggests high crystallization rates for the hard blocks from the melt, in contrast

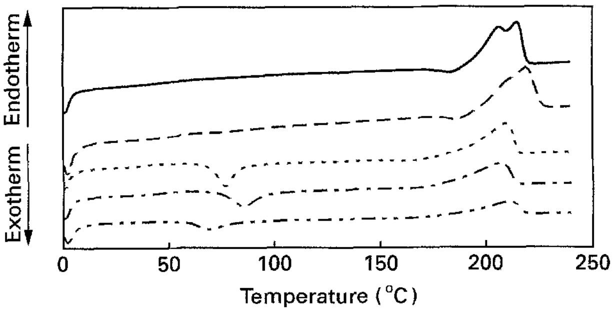

Figure 1 DSC traces for NBC at various polyether polyol prepolymer concentrations (% w/w) : ——, 10; — —, 20;- - - - , 30; — -, 40; — - -, 50.

with the materials with high soft block concentrations. This is likely to happen when the polyamide section of the chain, which is present as the major component, forms the outer continuous phase in these compositions. Partial crystallization therefore takes place during the cooling process. The morphologies of the metastable crystals so formed give rise to further crystallization (recrystallization) during the melting process, as evidenced by the weak exothermic peaks at ca. 185 °C for the 10 and 20% materials. The DSC results for the annealed NBC are shown in Fig. 2. All the aforementioned exothermic crystallization peaks are not observed in these thermograms, indicating somewhat better ordered structures in these samples, as discussed earlier. Further crystallization of hard blocks is not expected after annealing at 135 °C for 17 h.

All the DSC results suggest that the morphology of NBC varies with the composition and thermal history of the material. Phase inversion could possibly take place at compositions containing 20–30% w/w of polyether polyol prepolymer. However, it should be noted that in an incompatible two-phase system, the component present in the larger volume tends to form the continuous phase, whilst the minor component forms the disperse phase. During phase inversion, the different phases are not easily defined, and both components may be present as a co-continuous phase. In our present system, for example, at a given weight composition, the volume of hard blocks may change in the copolymer depending on the extent of crystallization, whilst the volume of the amorphous soft blocks remains fairly constant. Therefore, the phase inversion composition may change and depend on the thermal history of the copolymer or processing conditions. This will be discussed in more detail later (Section 4.2.2).

4.2. Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical spectroscopy is known to be sensitive to the molecular motion in polymers, making it possible to examine the different morphologies of NBC by this technique. In studying a polymer, dynamic experiments yield both the elastic modulus, or storage modulus, of the material and its mechanical damping, or energy dissipation characteristics. These properties are determined as functions of temperature and frequency (time). Below the glass transition temperature (T_g) of the material, the amorphous chain conformations are frozen into a rigid network, yielding a high value for the elastic modulus (E') and a low value for the loss tangent ($\tan\delta$). The T_g marks the onset of long-range motions of amorphous polymer chain segments, and is characterized by a large decrease in E' and a pronounced $\tan\delta$ peak.

4.2.1. Virgin NBC

The DMTA results for virgin samples are shown in Figs 3 and 4. The loss factor ($\tan\delta$) and elastic modulus (E') are plotted against temperature at a constant frequency of 1 Hz. Fig. 3 shows that there are two T_g for all the materials. The lower ones, which range from -58 to -50 °C, correspond to the T_g of polyether soft blocks, whilst the higher ones, which range from 13 to 25 °C, correspond to the T_g of nylon 6 hard blocks. The occurrence of two T_g, which correspond to the T_g of parent materials, indicates the incompatibility of these components of different chemical nature [1, 2, 6]. The $\tan\delta$ peaks for soft blocks are relatively narrow and their positions vary only slightly compared with those for the hard blocks. This observation stems from the fact that the polyether soft blocks are amorphous, and the copolymer chain growth is confined to the polymerization of caprolactam. The polyether block size and length could be regarded as constant, and their T_g would not

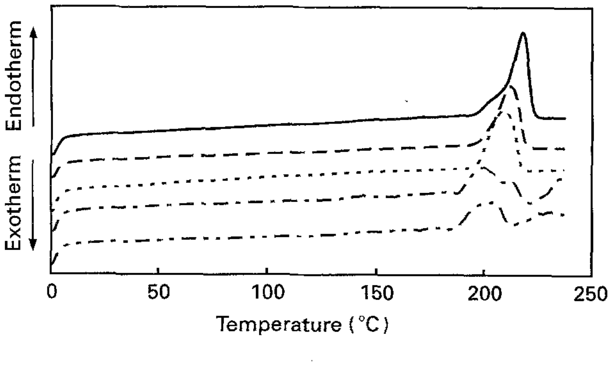

Figure 2 DSC traces for annealed (135 °C, 17 h) NBC at various polyether polyol prepolymer concentrations (% w/w): ——, 10; — —, 20; – – – –, 30; — -, 40; — – –, 50.

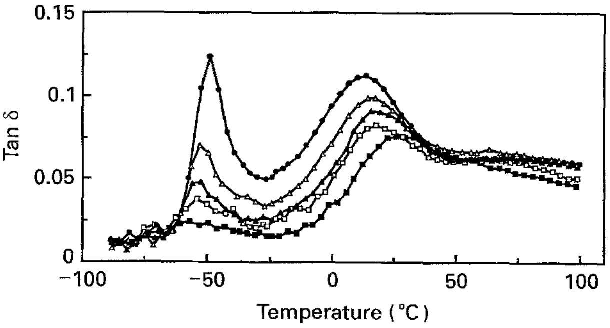

Figure 3 Variation of loss factor, $\tan\delta$, with temperature for virgin NBC at various polyether polyol prepolymer concentrations (% w/w) : ■, 10; □, 20; ▲, 30; △, 40; ●, 50.

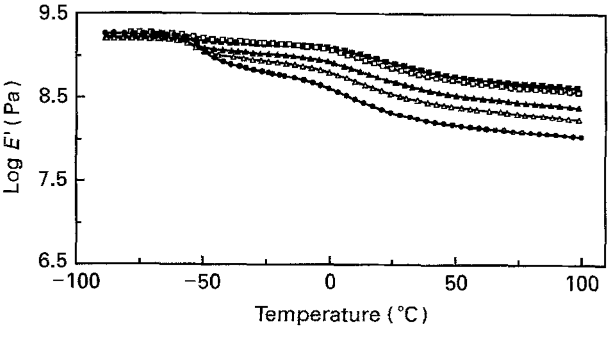

Figure 4 Variation of dynamic elastic modulus, E', with temperature for virgin NBC at various polyether polyol prepolymer concentrations (% w/w) : ■, 10; □, 20; ▲, 30; △, 40; ●, 50.

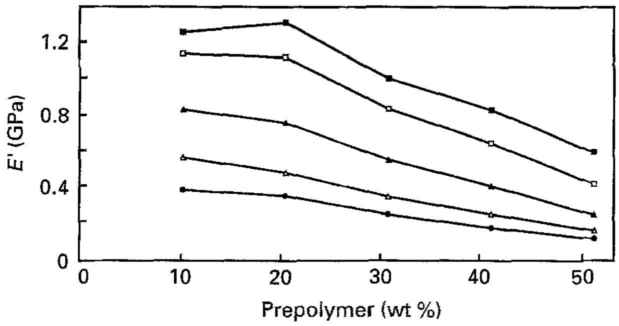

Figure 5 Variation of dynamic elastic modulus, E', with polyether polyol prepolymer concentration for virgin NBC at various temperatures (°C) : ■, − 20; □, 0; ▲, 20; △, 50; ●, 100.

be much affected by the differing compositions of the block copolymers. However, the crystallizable polyamide hard blocks are generated during the chain extension processes. Their block lengths are dependent on the copolymer composition [6]. It can be seen in Fig. 3 that there is a downshift of the T_g of hard blocks with increasing prepolymer concentration (decreasing polyamide concentration). The relatively pronounced shift in the T_g of hard blocks suggests changes in morphology with copolymer composition. This could be due to differing extents and rates of reaction, hence affecting the domain size and crystallization kinetics of hard blocks during copolymerization [6, 9]. It is believed that the nylon α transition involves the rupture of intermolecular hydrogen bonds among the polyamide chains [10]. The more ordered the chain structure, the more thermal energy (higher temperatures) will be required to dissociate these hydrogen bonds. As a result of the relatively fast kinetics of the polymerization, the polyamide hard blocks are formed and frozen in a thermodynamically non-equilibrium state during the reaction, especially when the polyamide is the minor component and forms the disperse phase which results in a lower T_g.

Apart from the changes in morphology with composition, the lowering of nylon T_g with increasing prepolymer concentration could also be due to the plasticizing effect of moisture [6, 11]. Gabbert and Hedrick [12] reported that the polyether polyol prepolymer could increase both the rate and amount of water absorbed into the block copolymer by hydrogen bonding compared with pure nylon 6. The downshift of nylon T_g with increasing polyether concentration could therefore also be the result of differences in moisture content in the materials.

It has been mentioned earlier that the T_g of a polymer is characterized by a large decrease in its dynamic elastic modulus. Since the NBC exhibits two T_g, one may expect this to be reflected in the temperature dependence of the elastic modulus, as shown in Fig. 4. It can be seen that, at very low temperatures, i.e. below the T_g of polyether, the corresponding E' for all the samples are similar to each other. As the temperature increases, the curves become divergent. In general, the higher the hard block concentration in the material, the higher is the corresponding E', i.e. the effect of hard blocks is to provide the crystalline phase which gives rise to high heat-sag resistance.

Fig. 5 shows the variation of E' with copolymer composition at different temperatures. The modulus of the material decreases with increasing soft block concentration. The incompatible two-phase system for the NBC is revealed by these sigmoidal curves in which the greatest slope can be found invariably at compositions 20–30% w/w of prepolymer for all temperatures, suggesting phase inversion at this region [2, 6]. It is generally accepted that in phase-separated systems, the component present in the largest volume tends to form the continuous phase and control the property plateau. The isolated inner phase is less effective, or its contribution greatly restricted. Material properties do not vary linearly with composition. The shape of the resulting sigmoidal curve is also affected by the morphology of the system [13]. It has been suggested earlier (Section 4.1) that, when the prepolymer concentration is < 20%, the continuous phase is composed of rigid polyamide hard blocks. The copolymers exhibit relatively high E' values (Fig. 5). At higher prepolymer concentrations, the soft blocks form the continuous phase with polyamide as the disperse phase, and the modulus decreases rapidly with increasing soft block concentration.

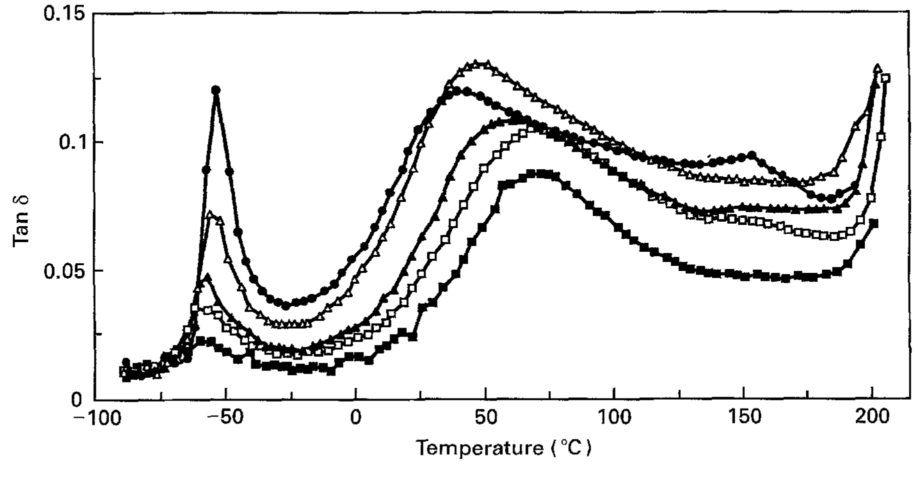

Figure 6 Variation of loss factor, tan δ, with temperature for annealed (135°C 17 h) NBC at various polyether polyol prepolymer concentrations (% w/w) : ■, 10; □, 20; ▲, 30; △, 40; ●, 50.

4.2.2. Annealed NBC

The structure/property relationships of NBC were further investigated by annealing the virgin materials as described in Section 3.1.2. It was believed that the virgin materials were not in a thermodynamic equilibrium state after copolymerization because of the fast kinetics of the system. Annealing the sample at 135 °C for 17 h could possibly increase the crystallinity and improve the crystal structure of the hard blocks, hence enhancing the performance of the material. This temperature was adopted because the polyamide homopolymer exhibits the maximum rate of crystallization in this temperature region [14, 15]. The DMTA results for the annealed samples are shown in Fig. 6. It can be seen that the T_g of soft blocks, ranging from -60 to -52 °C, are very similar to those for the corresponding virgin materials because of their amorphous nature, but the T_g of hard blocks, ranging from 40 to 71 °C, have shifted to higher temperatures, and their α transition peaks have become more diffuse, showing the change in morphology after annealing (Figs 3, 6 and 7). Studies on rubber-toughened nylon 6 composites [16] have shown that the shape and position of the α peak for the rubber component remained unchanged after annealing, but the nylon α peak shifted to a higher temperature. The diffuseness and upshift of the nylon α peak could be due to the morphology changes after annealing. The increase in crystallinity and the higher order of hydrogen bonding structure had restricted the motion of the amorphous polyamide chains.

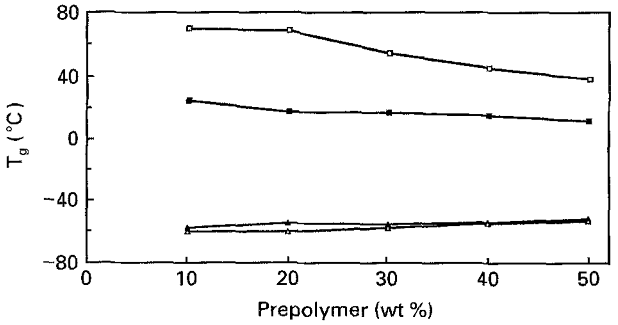

Figure 7 Variation of T_g of soft and hard blocks with polyether polyol prepolymer concentration for NBC before and after annealing at 135 °C for 17 h. ■, Hard blocks (before); □, hard blocks (after); ▲, soft blocks (before); △, soft blocks (after).

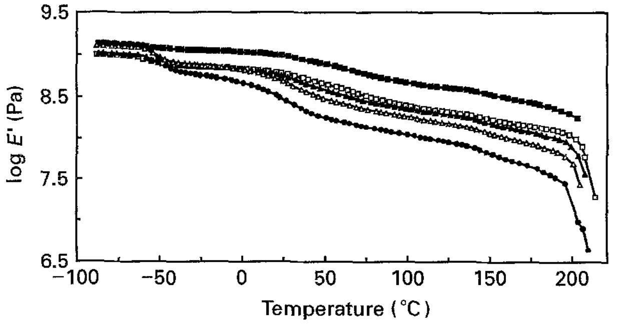

Figure 8 Variation of dynamic elastic modulus, E', with temperature for annealed (135 °C 17 h) NBC at various polyether polyol prepolymer concentrations (% w/w) : ■, 10; □, 20; ▲, 30; △, 40; ●, 50.

The temperature dependent elastic modulus curves show a similar trend as that for the virgin materials (Fig. 8). The higher the hard block concentration, the higher are the elastic modulus and the onset melting temperature. Fig. 9 shows the variation of E' with copolymer composition for the annealed samples at different temperatures. The greatest slope of the curve can now be found at compositions containing 10–20% w/w polyether prepolymer as opposed to 20–30% w/w for the virgin samples. Phase inversion occurs at a lower prepolymer concentration probably because of the volume contraction of hard blocks which has been brought about by the improved polyamide crystal structure after annealing, the volume of amorphous polyether soft blocks remaining relatively unchanged, as mentioned earlier in Section 4.1. The polyamide chains, which were present in the co-continuous (or continuous) phase, have inverted to the inner disperse (or co-continuous) phase.

The morphology changes brought about by annealing can have pronounced effects on the performance of NBC. This can be demonstrated by comparing the E' of the copolymers before and after annealing as shown in Fig. 10. One may expect that when the T_g of a polymer shifts to a higher temperature because of the higher order of crystal structure, the corresponding E' in the temperature range between the original and the new T_g (ca. 10–70 °C for the polyamide hard blocks in NBC) will also increase. This was generally true for NBC, except the 20% material. There was

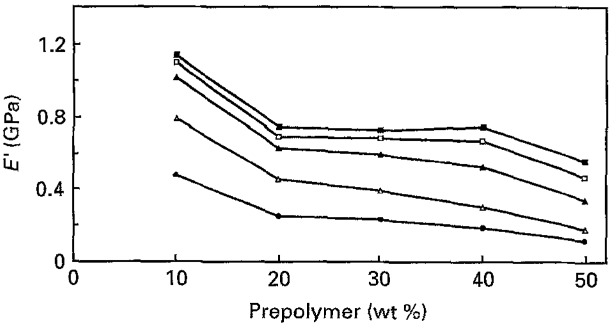

Figure 9 Variation of dynamic elastic modulus, E', with polyether polyol prepolymer concentration for annealed (135 °C 17 h) NBC at various temperatures (°C) : ■, − 20; □, 0; ▲, 20; △, 50; ●, 100.

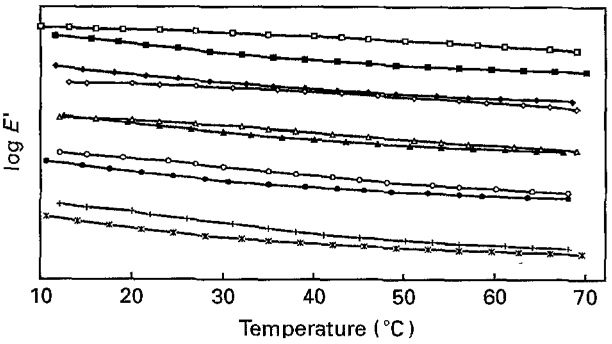

Figure 10 Comparison of the performance of NBC at various polyether polyol prepolymer concentrations before and after annealing at 135 °C for 17 h (% w/w) : ■, 10 (before); □, 10 (after); , ◆, 20 (before); ◇, 20 (after); ▲, 30 (before); △, 30 (after); ●, 40 (before); O, 40 (after); *, 50 (before); +, 50 (after).

a general decrease in E'after annealing. The result was unexpected, but can be explained by the shift in phase inversion composition as mentioned before. The hard blocks, which have previously been present in the continuous phase, become the less effective inner component of these block copolymers. It is known that the morphology of a polymer varies with its processing conditions. Crystallinity, for example, depends much on the thermal history of the material. When dealing with an incompatible multi-component system, such as NBC, the change in morphology may cause phase inversion. This, in turn, may cause an undesirable change in material properties as described earlier. Therefore, when handling a material at such sensitive compositions, one must be well aware of the morphology changes with the fluctuation in processing conditions. Reproduceability of product properties can only be guaranteed with properly controlled processing conditions.

5. Conclusions

DMTA results show that there were two T_g, corresponding to the T_g of polyether and nylon 6, for all the NBC samples in the work. This suggests that the polyether soft blocks and the polyamide hard blocks are incompatible. The results also reveal that, in general, the higher the hard block concentration, the higher the dynamic elastic modulus for the material, showing the effect of hard blocks which provided the heat-sag resistance to the copolymer. Furthermore, the temperature-dependent elastic modulus results also suggest that the disperse/continuous phase inversion could occur at compositions containing 20–30% w/w of polyether polyol prepolymer. This proposition was supported by the DSC results. The polyamide hard blocks in the annealed samples had a T_g higher than those for the corresponding virgin materials, probably because of the better ordered crystal structure, and for this reason, E' increased for all the samples apart from the 20% material. The lowering of E' for this sample could be due to the volume contraction of hard block domains, hence shifting the phase inversion composition to 10–20% w/w of prepolymer. The hard blocks, which had previously been present in the continuous phase, became the less effective inner disperse phase. Therefore, when dealing with NBC at compositions close to those where phase inversion might be possible, great care must be taken to maintain the processing conditions in order to achieve the desired material properties.

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