Synthesis and properties of polyurethanes based on polyolefin: 3. Monitoring of phase separation by dielectric relaxation spectroscopy of segmented semicrystalline polyurethane prepared in bulk by the use of emulsifiers

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Semicrystalline segmented polyurethanes based on hydrogenated polybutadiene soft segments (H-PBD) and butanediol (BDO) as chain extender were synthesized in bulk. Because of the initial immiscibility of the reactants, macroscopic phase separation occurs during a two-step polymerization in bulk. As a previous work on the same materials prepared in polar solvent has shown the high level of microphase separation with such polymers, the challenge of the present work is also to obtain a high level of microphase separation for bulk-prepared polyurethanes. For this purpose the synthesis of polyurethanes in bulk is carried out in the presence of different emulsifiers to minimize the effects of the premature macrophase phenomenon. The morphology of such polyurethanes with non-polar soft segments can be well characterized by dielectric measurements. The dielectric relaxations confirm the thermal behaviour and also the presence of a mixed interfacial region. The addition of emulsifiers to bulk samples decreases the number of short isolated or amorphous hard segments, as shown by size exclusion chromatography results, and suppresses the related conduction process appearing in the dielectric measurements. The results show the control of the structures by appropriate synthesis and the monitoring of phase separation using dielectric spectroscopy.

(Keywords: semicrystalline polyurethanes; emulsifiers; microphase)

INTRODUCTION

Segmented polyurethanes (PUs) are linear block copolymers which are obtained from the reaction of three monomers: a macroglycol, a diisocyanate and a low-molecular-weight diol.

The macroglycols are hydroxy-terminated polyesters, polyethers and more recently polyalkyls or polysiloxanes. They form the soft segments of the PU chain. The hard segments are essentially urethane oligomers of two monomers; diisocyanates and diols, which are connected to soft segments through urethane linkages. Diisocyanate 4,4′-methylene *bis* (*p*-phenyl isocyanate) (MDI) and 1,4-butanediol (BDO) are the most commonly used diisocyanate and chain extender.

These segmented PUs can be polymerized under a wide variety of conditions leading to different distributions of the molecular weight, hard segment length and composition and consequently sample properties and morphologies.

The morphological complexity of segmented PUs can be interpreted by taking into account the domain formation due to the segregation phenomena on different levels. First, the macrophase separation appears because of the initial immiscibility[1–3] or immiscibility appearing during the reaction[4–6] in bulk of the reactants. Speckhard and co-workers[7–10] have developed a Monte Carlo simulation utilizing several simplifying assumptions proposed previously by Peebles[11,12]. They have proposed a model which allows the exploration of the potential effects of premature phase separation on the molecular weight and composition parameters.

Second, the microphase separation on the molecular scale is due to the thermodynamic immiscibility between the hard and soft segments of the PU chain which produces a phase-separated morphology of hard-segment-rich and soft-segment-rich phases. This two-

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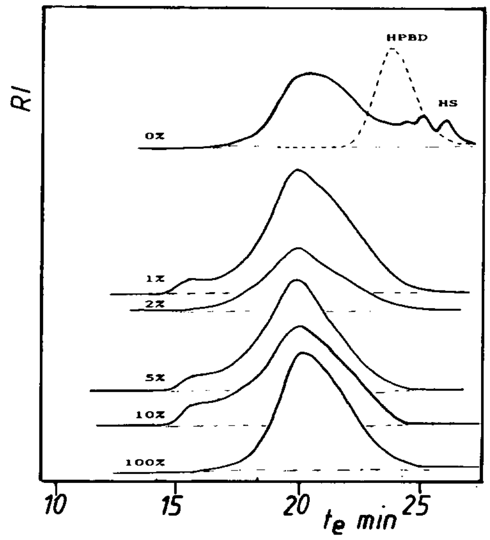

Figure 1 S.e.c. chromatograms for PUs prepared in bulk with different amounts of multiblock emulsifier E. 100% E, PU obtained in solution; 0% PU, bulk PU without emulsifier

phase structure gives rise to the interesting and useful properties of these materials. For example, polyalkyl-based PUs[3] exhibit a high level of macrophase separation when they are prepared in bulk (opaque sample) and a high level of microphase separation when they are prepared in solution under homogeneous conditions (single hard- and soft-segment T_g values were observed). In this last case macroscopic phase separation during a two-step polymerization in solution is suppressed by using a suitable solvent. The samples were transparent to light and completely soluble in THF.

The aim of this work on hydrogenated polybutadiene-based PUs is to control the morphology of such bulk-prepared PUs.

To get better insight and understanding of the microphase separation phenomena a previous paper[13] reported on the synthesis and properties of amorphous segmented PUs based on hydrogenated polybutadiene, synthesized under homogeneous conditions in a polar solvent to prevent any premature macroscopic phase separation. Differential scanning calorimetry (d.s.c.) studies of the glass transition, T_g, have shown two glass transitions in the case of these amorphous segmented H-PBD PUs: a soft phase T_g(S) and a hard phase T_g(H). These two-phase PU materials, considered as model systems, have shown molecular rearrangements under thermal treatments and a degree of phase separation of the soft segment determined to be in the range of 85–95%. An understanding of their properties and related behaviour has helped in further investigations on more complex morphologies of PUs with semicrystalline hard segments.

A second paper[14] has presented in particular a comparison of the properties of a semicrystalline PU produced using the same formulation but prepared by different processes including preparation in good solvent, in a non-suitable solvent, with or without catalyst and in bulk. Such different routes of preparation induce various characteristics.

Size exclusion chromatography (s.e.c.) measurements indicate (*Figure 1*) the different distributions of the molecular weight and the presence of short isolated hard segment especially in the case of samples prepared in bulk.

Dielectric spectroscopy has been shown to be a complementary technique to viscoelastic spectroscopy and small angle X-ray scattering (SAXS) to obtain morphological information. Dielectric results confirm the thermal behaviour and show two relaxations related to the soft phase of the materials and the presence of a mixed interfacial region. The mixed-phase relaxation is very sensitive to the type of synthesis and consequently to the induced morphology in the material. Additionally the appearance of a conduction peak is correlated to the presence of the isolated hard segments.

One of the most attractive routes for blending two immiscible oligomers or polymers is the use of emulsifiers. In its simplest form, the emulsifier comprises blocks which are chemically identical to the respective components of the blend, although non-identical segments which are miscible or partially miscible with the corresponding homopolymers should work equally well to promote a finer and more stable dispersion of the phases during mixing[15].

This paper describes how emulsifiers can improve the synthesis and properties of segmented semicrystalline PUs prepared in bulk. We have used two types of block copolymers[16]. The first is a segmented polyurethane (E) obtained in solution under homogeneous conditions. Another (B) is a triblock copolymer based on monofunctional poly(ethylene oxide) (PEO). The advantage of PEO is that it is miscible with the diol BDO. Different molecular weights ($\overline{M}_n = 350$, 750, 5000) of monofunctional PEO were used.

EXPERIMENTAL

Materials and synthesis

The hydrogenated polybutadiene oligomer (H-PBD; Nippon Soda; $\overline{M}_n = 2100$, $\overline{F}_n = 1.8$; 18% ethylene; 82% butene) was degassed at 60°C for 24 h before use. Pure MDI (Bayer) and BDO (Aldrich) were used as received.

The multiblock copolymer, E, is a segmented polyurethane (H-PBD–MDI–BDO 1/3/2) obtained in tetrahydrofuran (THF) solution under homogeneous conditions as described previously[14]. It has a high molecular weight, $\overline{M}_n \approx 25\,000$ (based on polystyrene standards).

Emulsifiers, B, are triblock copolymers based on different PEO oligomers, $\overline{M}_n = 350$, 750 or 5000 (Aldrich). The synthesis is as follows: First, 1 mol of H-PBD reacts in bulk with 2 mol of MDI at 80°C to give MDI–H-PBD–MDI and MDI in excess after total reaction confirmed by s.e.c. analysis. By s.e.c. it is also possible to determine the fraction of unreacted MDI. Due to the fact that the reactivity of the two isocyanate groups is not very different some chain extension reactions occur and the fraction of unreacted MDI is 0.25, compared with the theoretical one, 0.16. Then, 2 mol of monohydroxy PEO are added at 120°C to obtain what is termed the triblock, PEO-MDI–H-PBD–MDI-PEO. In fact this triblock is not pure because there is always a fraction of trimer PEO–MDI–PEO due to the excess of MDI and a fraction of H-PBD–MDI–PEO due to the monofunctional HPBD ($F_n = 1.8$). These impurities explain the dissymmetry of the molecular weight distribution curves (see for example *Figures 2* and *3*).

Due to the high viscosity of a linear segmented PU, the blend of oligomer H-PBD with the emulsifier E is

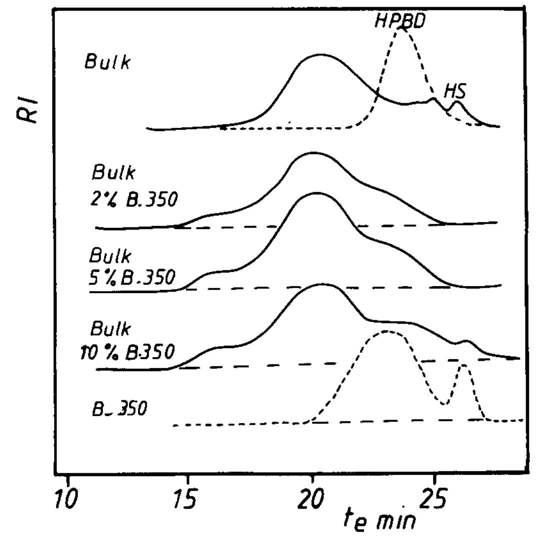

Figure 2 S.e.c. chromatograms for PUs prepared in bulk with different amounts of triblock emulsifier B350

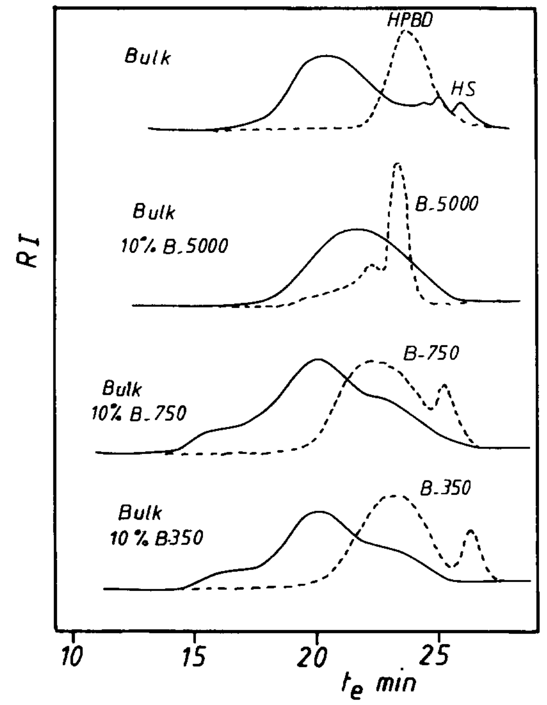

Figure 3 S.e.c. chromatograms for PUs prepared in bulk with 10 wt% triblock emulsifier B with different molecular weights for PEO blocks

performed in THF at 25°C and it is dried in vacuum at 60°C for 4 h. The blend of oligomer H-PBD with the emulsifier B is obtained more easily by stirring at 80°C in bulk for 2 h. This type of process without solvent is preferred from an industrial point of view.

The PU synthesis in bulk was carried out with these blends by a conventional two-step method. The procedure was as follows: (1) in the first step of the polymerization the blend is end-capped with an excess of MDI in bulk at 80°C for 4 h under vacuum; (2) in the second step, chain extender was added. The reaction mixture was then mechanically stirred vigorously for 2 min, degassed and poured into a 1 mm thick mould. Curing was done at 110°C for 24 h. All samples were stored at room temperature for 20 days before testing.

The materials have 29 wt% of hard segments and the names of the polyurethanes will indicate the amount of emulsifier E or B as well as the molecular weight of the emulsifier B block based on PEO.

Experimental methods

A Waters HPLC apparatus equipped with refractometric (RI) and ultra-violet (u.v. at 254 nm) detectors was used for s.e.c. analyses. Microstyragel columns with 1000, 500 and 100 Å pore sizes were used. The solvent (THF) flow rate was 1.5 ml min^{-1}. All molecular weights reported are based on a calibration curve from polystyrene standards.

A Mettler TA 3000 microcalorimeter was used for the d.s.c. measurements. The d.s.c. runs were performed under argon using a heating rate of 7.5 K min^{-1}. The glass transition temperature was taken as the onset of the phenomenon.

Dielectric measurements were carried out with a Polymer Laboratory cell connected to Hewlett Packard 4274A and 4275A multifrequency LCR meters. The measurements were performed in the temperature range −70°C to +180°C and using frequencies of 100 Hz to 100 kHz with a heating rate of 1°C min^{-1} under dry nitrogen.

RESULTS AND DISCUSSION

Molecular weight (M_w) *and molecular weight distribution* (MWD)

The first results of the synthesis in bulk have been described in a previous work[14] and have shown that the materials obtained were opaque and partially soluble in THF. The initial H-PBD oligomer and also lower molecular weight species were clearly evident on the s.e.c. trace (*Figure 1* or *Figure 2*, 0%). These lower molecular weight species are isolated short hard segments which are present due to the stoichiometric imbalance in both phases during the polymerization of the initially heterogeneous system. As reported by Miller *et al.*[8–10], premature phase separation leads to a broadening of the composition distribution and the molecular weight distribution and also leads to a limiting of the degree of polymerization.

During the synthesis of PU with emulsifier E, the initial viscosity increases with the amount of emulsifer but the opacity of the final polymer decreases. Emulsifiers B, with lower molecular weight than E, were prepared to decrease the initial viscosity of the reactive system. In fact this viscosity is similar with or without the addition of B but all the samples were opaque.

The s.e.c. results are given in *Figure 1* and *Table 1* (expressed in PS standards for a comparison) for the PUs prepared with emulsifier E and in *Figures 2* and *3* for the PUs prepared with emulsifier B, with different amounts of emulsifier or for different molecular weights of the PEO triblock. All these samples were partially soluble in THF, which is proof of the heterogeneity in the composition. The insoluble fractions are attributed to chains rich in hard segments.

The figures demonstrate that PUs prepared in bulk, but with different percentage of emulsifier E or B, always have a broad molecular weight distribution, but without identified isolated hard segments. This fact seems very important for the dielectric properties (see below).

Table 1 S.e.c. results of PU obtained with emulsifier multiblock E (% E, during the synthesis in bulk)

% E	Solubility in 100% THF	$\overline{M_n}$	$\overline{M_w}$	M_w/M_n
100	Yes	24 900	54 800	2.2
10	No	15 270	167 750	11.0
5	No	21 500	150 700	7.0
2	No	20 500	84 700	4.2
1	No	15 000	106 600	7.2

Molecular weights are based on PS standards

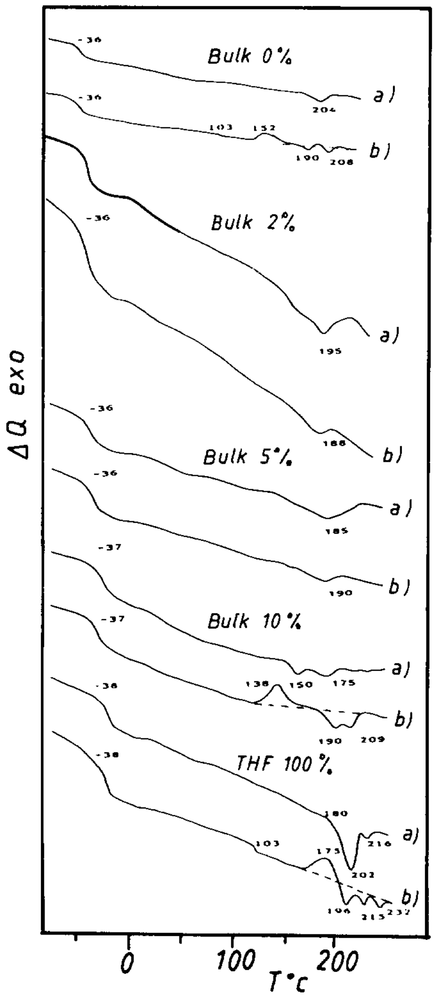

Figure 4 D.s.c. curves for bulk PUs with or without different amounts of emulsifier E (segmented PU 1/3/2 prepared in THF). (a) First scan up to 250°C; (b) second scan after quenching to −150°C

For all the samples the shape of the elution peaks at the high molecular weights are also characteristic of a reaction in a two-phase system. The large heterogeneity in the molecular weight distribution (*MWD*) explains the large variation, 2.2 in solution to 11 in bulk, in the polydispersity index $\overline{M_w}/\overline{M_n}$.

The dissymmetry of the *MWD* is more important in the case of polymerization in the presence of triblocks. This behaviour can be explained by the presence of the triblock and by the triblock composition with PEO–MDI–H-PBD–MDI–PEO oligomers but also with some PEO–MDI–PEO and H-PBD–MDI–PEO contents, as explained above. For this reason we have not calculated $\overline{M_n}$ and $\overline{M_w}$ in this case. In conclusion, it can be stated that:

(1) For E, 1% or 2% are effective and sufficient.

(2) For B, it is not necessary to have PEO blocks with high M_w, B-350 can be a good emulsifier, and here too, 2% of B in the PU synthesis is sufficient.

Transition of hard and soft phases

The glass transitions of the soft and hard blocks and the transitions of the semicrystalline hard blocks were investigated using d.s.c. The thermograms are shown in *Figures 4* and *5*, respectively, for the bulk PUs with the multiblock emulsifier E and the bulk PUs with the triblock emulsifier B.

Compared with the samples prepared in homogeneous solution in THF, the PU prepared in bulk seems to be less organized, the hard phase is quite amorphous, and the calculated segregation ratio of the soft segment[14] is 80% instead of 85–95% for the latter one.

The glass transition of the hard microphase is only detectable in the region 90–110°C during a second heating scan after a quenching from the melting temperature of the hard microdomains and only in the case of the triblock emulsifiers. In the case of multiblock emulsifier it seems that the hard microphase glass transition is hidden by the first exotherm which can correspond to an organization of hard segments. With triblock emulsifier B350, the T_g of the hard phase decreases from 103 to 90°C due to a plasticization effect of the hard phase by the PEO blocks 350 and to lower temperature when the molecular weight of the PEO blocks increases.

Concerning the high temperature domain, two or three

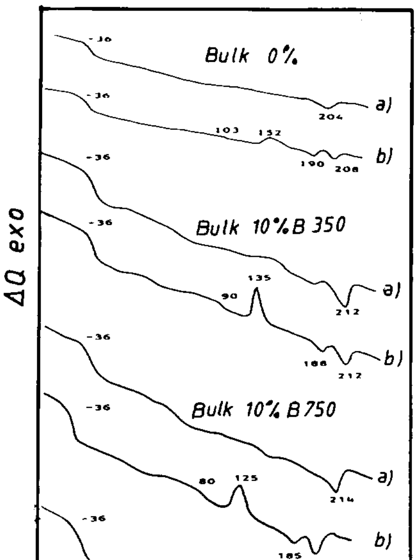

Figure 5 D.s.c. scans for bulk polymerized segmented PUs with 10% triblock copolymer PEO/HPBD in the formulation: influence of the molecular weight of PEO blocks. (a) First scan up to 250°C; (b) second scan after quenching to −150°C

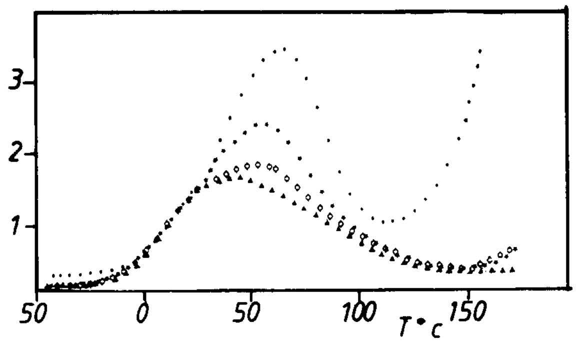

Figure 6 Dielectric relaxations (1000 Hz) of segmented PUs based on H-PBD-MDI-BDO prepared in bulk (●) and with 2% (ϕ) or 10% (*) of emulsifier E. Emulsifier E is a segmented PU 1/3/2 prepared previously in THF (▲) (multiblock E)

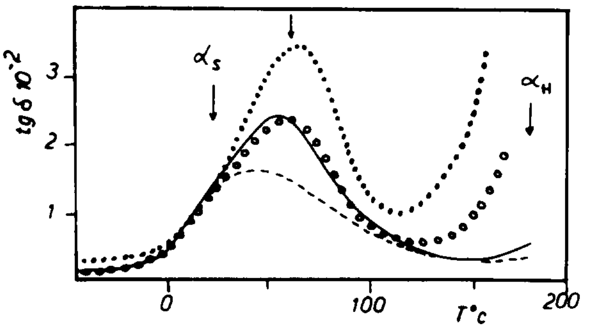

Figure 7 Dielectric relaxations (1000 Hz) of bulk polymerized segmented PUs prepared with triblock copolymer B350. (●) Bulk 0%, (○) 2%. Dielectric spectra of (——) PU 1/3/2 with 2% multiblock E or (---) PU 1/3/2 prepared in THF are plotted for comparison and discussion

hard segment melting peaks are visible. As mentioned before, in the literature regarding PUs based on BDO, the two endotherms observed at about 190–200°C and at 200–240°C are ascribed to two different degrees of organization: a paracrystalline structure with preferential orientation in the chain (small-scale ordering) and a pure spherulitic organization[17–20]. Moreover, these two structures appeared to be dependent on each other: the first one can generate the second one according to the imposed thermal treatments[19,21–24]. A phenomenon of nucleation growth can explain the observed peak of recrystallization in the melting zone of the paracrystalline structure of a second thermal treatment.

In addition to these morphological phenomena, chemical rearrangements occur depending on the instability of the urethane bonds when the temperature exceeds 180°C. These rearrangements induce segment redistributions and chain scissions. The formation of long isolated hard segments that would favour a better hard-segment organization is not excluded.

When the M_w of the PEO blocks of the emulsifier B is too high, for example B5000, and when the percentage of PEO block in hard domains is too high, the hard domains are quite amorphous.

Interphase and dielectric properties

The dielectric relaxations at a frequency $N = 1000$ Hz for the PUs prepared in bulk with different contents of the emulsifier E and in solution (pure E) are given in *Figure 6*. The broad relaxation peak attributed to the mixed interfacial region[14] decreases as the emulsifier content during the bulk synthesis increases. The most important feature is that the conduction process at high temperatures ($T > 120$°C) resulting from isolated hard segments in the bulk sample disappeared when 2% of the emulsifiers are introduced during the synthesis. This behaviour has to be compared with the s.e.c. results on the same product which point to the same conclusion. In fact, the isolated hard segments, when they are present in the sample, are able to move under the electric field and contribute to a conduction phenomenon. This conduction process could have a bad consequential effect in use, and the fact that it disappeared when the PU is prepared with emulsifier is promising for future applications.

In *Figure 7* we compare the dielectric properties of the segmented PU based on H-PBD–MDI–BDO (1-3-2) prepared in bulk or in solution (product 100%) with or without the addition of emulsifier B prepared with PEO-350.

The decrease in amplitude of the relaxation peak is comparable to the preceding case with emulsifier E except that the conduction is not decreased as much with 2% of emulsifier B350 as with 2% of emulsifier E, the dielectric spectra of which are also shown in *Figure 7* for global comparison and discussion of all the samples. At high temperatures ($T > 120$°C), *Figure 7* reveals clearly that the conduction process is not as well attenuated with emulsifiers B as with E. Thus the effect of the addition of E or B in the synthesis of the PUs prepared in bulk plays an important role on the organization of the mixed interfacial region involved in this relaxation.

Some differences are to be noticed also in the thermal stability of the dielectric losses above 150°C in the case of PU prepared in the presence of emulsifier B. In fact, *Figure 8* shows that this increase of the dielectric loss is related to the glass transition of the hard segment. As the molecular weight of PEO increases ($\bar{M}_n = 750$ or 5000), this effect becomes more evident because the relaxation α_H associated with T_g(H) is shifted to a lower temperature (*Figure 8*). This corroborates the fact that PEO-based emulsifier chains are involved in the hard domains of the material and plasticize the rigid phase. Therefore this effect limits the benefit of the use of the triblock copolymer B as compared to the multiblock E.

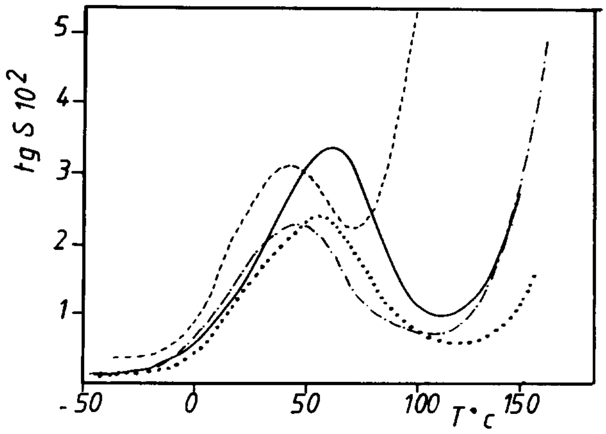

Figure 8 Dielectric relaxations of bulk polymerized segmented PUs prepared with 10% triblock copolymer PEO. Influence of the molecular weight of PEO block. (——) Bulk 0%; (●) B350; (—·—·) B750; (---) B5000

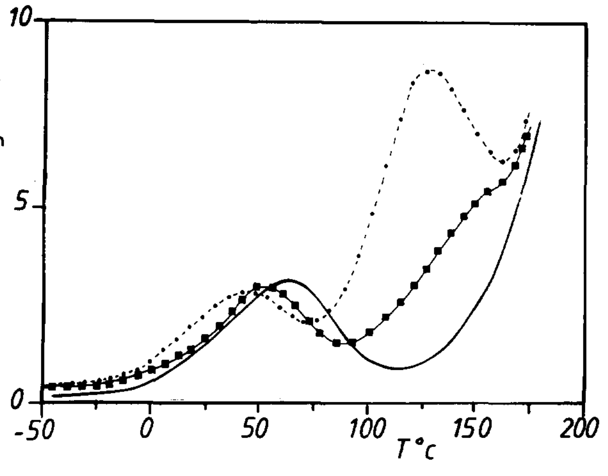

Figure 9 Dielectric relaxations (1000 Hz) of bulk polymerized segmented PUs prepared with emulsifier triblock copolymer B5000 (——) bulk 0%; (■) 5%; (—·—·) 10%

Other dielectric measurements are reported in *Figure 9* to demonstrate that when the plasticization effect of the hard domains is important it is possible to obtain a maximum in the relaxation α_H. In this case, it should be remembered that the d.s.c. results (*Figure 5*) indicated that the PU prepared with 10 wt% B5000 has an amorphous hard phase. Thus *Figure 9* demonstrates the PEO content effect on the plasticization phenomena and corroborates the previous d.s.c. results.

The activation energy of the α_H relaxation is about $E_a = 90\,\mathrm{kJ\,mol^{-1}}$. Compared with the level of the activation energy for the amorphous[13] or semicrystalline PUs[14] it seems that the PEO chain in the hard domain increases the mobility of the dipoles and favours their motions.

The three curves of *Figure 9* join above 150°C and the beginning of a conduction process can be attributed to an interfacial polarization in these heterogeneous materials.

In conclusion, the sensitivity of dielectric spectroscopy allows the evolution of the α' relaxation peak attributed to the mixed interfacial region to be correlated quite well with the phase separation appearing in such material and governed by the type of synthesis.

CONCLUSION

This paper has dealt with the control and minimization of the macrophase separation during synthesis in bulk of the system by introducing block copolymers as emulsifiers. These emulsifiers should decrease the interfacial tension between initial immiscible phases (rich prepolymer phase and rich BDO phase) and reduce the size of the dispersion.

For the two families of emulsifiers used, multiblock copolymer PU 1/3/2 and triblock emulsifier based on PEO, we have shown that their addition to the reactants improves the synthesis by avoiding the formation of isolated short hard segments.

The interphase decreases as the percentage of emulsifier increases. Additionally, PEO emulsifiers plasticize the amorphous hard phase and embed its crystallization. This effect increases when the chain length and/or the quantity of PEO increase. The interphase is an important factor and its evolution is seen well by dielectric measurements which are very sensitive to the relaxation α' of this mixed phase.

The best control of macrophase separation and of the low dielectric losses at high temperature is obtained with the multiblock E as emulsifier. It must be remembered, however, that it produces a high viscosity due to high molecular weight and that it must be added to the PU samples in solvent, unlike the PEO-based emulsifier which can be incorporated directly.

This part has described the introduction of emulsifier in PU bulk synthesis to obtain materials with properties similar to, and sometimes even better than, those of PUs prepared under homogeneous or heterogeneous conditions in solution. Dielectric studies of these segmented PUs based on polyolefins have been presented for all types of PU (amorphous, semicrystalline)[25] to show relations between structure and dielectric behaviour. These PUs based on polyolefin are interesting materials with low moisture permeability, especially for adhesives and electrical coating applications, and they also offer a better resistance to oxidation than polybutadiene-based PUs.

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