# Dynamic mechanical thermal analysis of some well defined poly(ε-caprolactone)-*g*-poly(methyl methacrylate)-*co*-polyurethanes

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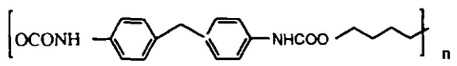
Dynamic mechanical thermal analysis of some well defined poly(ε-caprolactone)-*g*-poly(methyl methacrylate)-*co*-polyurethane samples has been performed. The results show that the hard segment/soft segment phase separation of the polyurethane backbone is decreased with soft segment grafting and that all of the poly(methyl methacrylate) is mixed in with the poly(ε-caprolactone). These results confirm previous differential scanning calorimetry studies.

**(Keywords: dynamic mechanical analysis; graft copolymers; polyurethanes)**

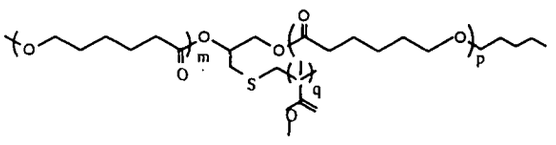
*Introduction*

The relaxation behaviour of polyurethanes (PUs) has been widely studied by a variety of techniques. In particular, dynamic mechanical techniques have proved useful in studies of the morphology and extent of phase separation in segmented PUs and composites of PUs with other polymers. A synthetic route to segmented PU polymers with polycaprolactone (PCL) soft segments and poly(methyl methacrylate) (PMMA) grafts located only in the PCL segments has been published by the authors[1,2]. These polymers have the hard blocks shown below:



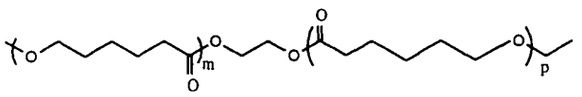

4,4'-diphenylmethane diisocyanate (MDI)/1,4-butanediol (BD) hard segment

The soft segments may contain a PMMA graft:




PCL-*g*-PMMA

or they may be linear:




Linear PCL

The synthesis was designed so that it was possible to predetermine the ratio of PCL-*g*-PMMA to linear PCL in the final polymer, so that PU-*g*-PMMAs with preset degrees of branching in the soft segment have been synthesized.

Differential scanning calorimetry (d.s.c.) of these polymers[3] showed that all of the PMMA branches are mixed into a homogeneous blend with some of the PCL. Phase separation between the hard segments and soft segments was shown to decrease as the PMMA content increased. We now present some dynamic mechanical thermal analysis (d.m.t.a.) data on these polymers.

Several studies of the dynamic mechanical properties of various combinations of PUs with acrylic polymers have been reported. Allen *et al.*[4] polymerized MMA which had been allowed to swell PU networks. These materials exhibited the relaxations attributed to PMMA. The soft-segment glass temperature, $T_g$, was present but it was shifted to higher temperatures in the presence of PMMA. They concluded that interactions occurred at the PU/PMMA interface. Epoxy/polyacrylate/PU interpenetrating networks (IPNs) were synthesized by Cassidy *et al.*[5]. They showed that grafting the polyacrylate polymer onto the PU produced materials in which the PU and PMMA were mixed at the molecular level. Considerable phase mixing was seen in PU/PMMA IPNs synthesized by Orashant and Suthar[6]. PU/poly(ethyl methacrylate) IPNs were studied by Fox and co-workers[7-9]. They showed that phase separation occurred but the two $T_g$s were shifted towards each other and the tan $\delta$ peaks were broader than in the homopolymers. The soft-segment $T_g$ was less affected than the PMMA $T_g$. Iannance *et al.*[10] used d.m.t.a. to study blends of PMMA and PCL. Their results indicate a limited compatibility between the two components.

*Experimental*

*Materials.* The PU-*g*-PMMAs, the linear PU and the PMMA diol were those synthesized as described in our previous publications[1,2]. The hard segments in the PUs are formed from MDI and BD. The PU-*g*-PMMAs have been given the following form of nomenclature: PU-*g*-PMMA *x*/*y*/*z*, where *x* denotes the weight percentage of hard segment in the PU backbone, *y* is the molecular

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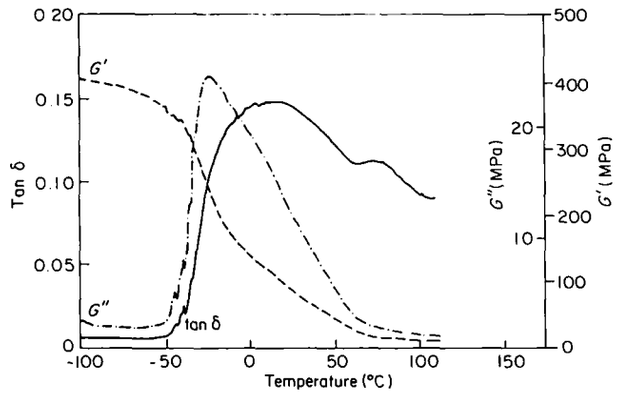


**Figure 1** D.m.t.a. spectra of PU30

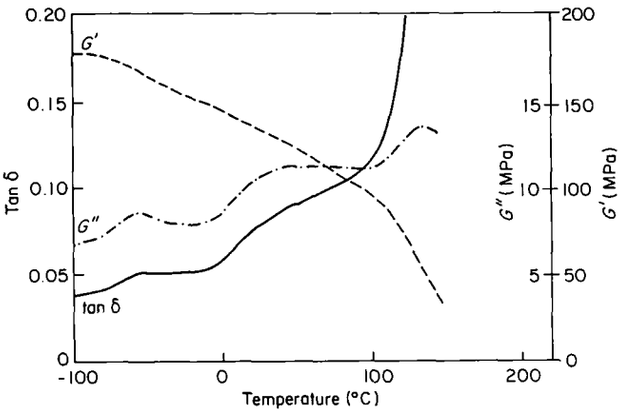


**Figure 2** D.m.t.a. spectra of PMMA, $M_n$ 12000

weight of the PMMA side chain and $z$ is the weight percentage of PMMA in the polymer. The PMMA diol has a number average molecular weight, $M_n$, of 12000 g mol$^{-1}$. It was used as a precursor in the preparation of the PU-*g*-PMMA polymers. The diol functionality takes the form of a 1,2-diol end group, at one end of the chain end only. The linear PU had a hard segment content of 30 wt% and hence was given the nomenclature PU30.

*Dynamic mechanical thermal analysis.* The PUs exhibited several decreases in the storage modulus, $G'$, which in total produced a decrease in sample stiffness outside the range which could be studied by the instrument. In order to study the polymers, therefore, the modulus change was decreased by coating the polymers onto glass fibre braids. This technique also had the advantage of using much thinner films so that solvent removal was easier.

Solutions of the polymers were made up (40 wt% solids) using dimethylacetamide as the solvent. The braids were 10 mm wide. Some 25 ml of the solution was applied per 10 mm of braid. Care was taken to avoid formation of pinholes or other voids. Once a braid had been successfully coated, the solvent was evaporated in an oven at 50°C. The solvent was slowly removed over a period of 11 weeks. After this time the braids were inspected and any films which were not continuous were discarded. Once satisfactory samples had been produced, d.m.t.a. was performed on them, as follows.

D.m.t.a. was performed on PU30, PU-*g*-PMMA 30/12000/25, PU-*g*-PMMA 30/12000/50 and PMMA diol 12000. A frequency of 5 Hz was used. The instrument was operated in the shear mode so that values of storage shear modulus, $G'$, loss shear modulus, $G''$ and tan $\delta$ were obtained. The temperature was raised at a rate of 5°C min$^{-1}$ between −100 and 150°C. A Polymer Laboratories instrument was used.

*Results and discussion*

D.m.t.a. spectra of the PU30 and PMMA diol 12000 linear polymers are shown in *Figures 1* and *2*. *Figures 3* and *4* show the two graft copolymers which were based on these polymers (i.e. PU-*g*-PMMA 30/12000/25 and 30/12000/50). In these polymers the fraction of PCL which was grafted was 0.1 and 0.6, respectively.

On going from low to high temperature the first thermal event observed in the PU30 sample was apparent as a sharp decrease in $G'$. The temperature of this transition corresponds well with the $T_g$ of the PCL segment ($\delta$ in our d.s.c. paper) as measured by d.s.c.[3]. The melting of the PCL crystalline phase was seen in the d.s.c.[3] as a sharp endothermic peak at 40°C and it was observed in $G'$ as a more gradual decrease between 0 and 50°C. The loss parameters show both these events as broad peaks encompassing both transitions, over the range −50 to 50°C. The highest temperature event seen in this sample is a tan $\delta$ peak at 75°C. The $G'$ and $G''$ plots do not show this feature. It is probable that this event is due to the hard-segment $T_g$. The d.s.c. results also showed a transition between 125 and 180°C which was designated $\alpha$ and is due to the break-up of hard-segment domains. In the d.m.t.a. experiment, this transition is seen as the end of the experiment since the relaxation involves a drop in $G'$ outside the range of measurement of the instrument.

*Figure 2* shows the d.m.t.a. spectrum of PMMA with $M_n = 12000$ g mol$^{-1}$. The transitions seen in this material are the PMMA $T_g$ at 110°C, as the onset temperature in $G'$ and 136°C as the peak in $G''$. A secondary relaxation is also seen at −52°C in both $G''$ and tan $\delta$. This relaxation has been assigned to the onset of rotation of the ester side-chain in PMMA[11].

The effects of grafting are shown in *Figures 3* and *4*. In both of these samples $\delta$ is the first thermal event

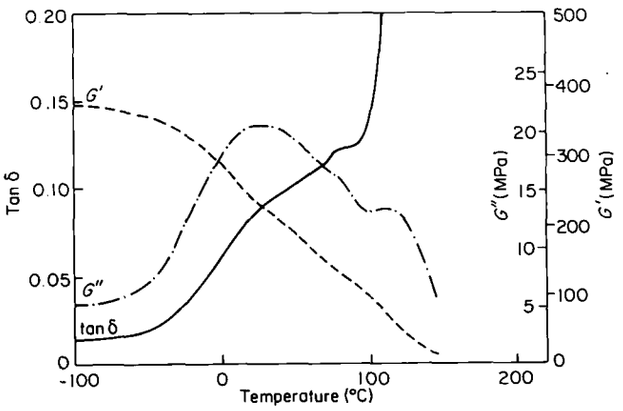


**Figure 3** D.m.t.a. spectra of graft copolymer PU-*g*-PMMA 30/12000/25

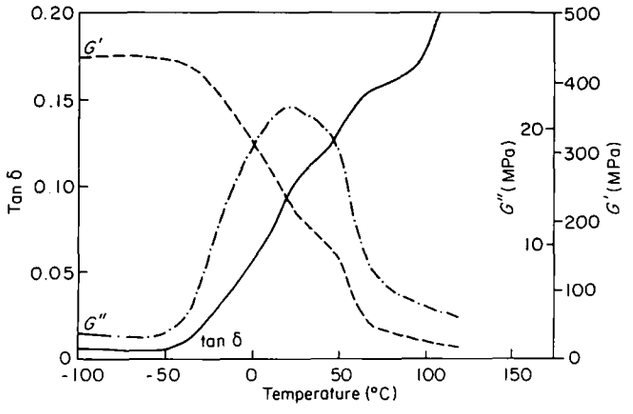


**Figure 4** D.m.t.a. spectra of graft copolymer PU-*g*-PMMA 30/12 000/50

observed. The onset temperature of $\delta$ occurs in $G'$ at $-50$°C in PU-*g*-PMMA 30/12 000/25 and $-45$°C in PU-*g*-PMMA 30/12 000/50. These results agree closely with the previously reported d.s.c. data for these polymers. In accordance with the d.s.c. data, this increase in tan $\delta$ with increasing PMMA content is interpreted as signifying increased mixing between the hard segments and soft segments. The wide temperature range over which $G'$ decreases indicates that several relaxation processes are involved in reducing $G'$ to its final value.

In our d.s.c. report[3], PCL crystallinity was seen in PU-*g*-PMMA 30/12 000/25 but not in PU-*g*-PMMA 30/12 000/50. This difference is not easily discerned in the d.m.t.a. data.

No evidence for the existence of a PMMA homophase $T_g$ was observable in these plots. If such a phase were present, one would expect to see a peak in $G''$ at 136°C and a sharp decrease in $G'$ at 110°C, as seen in *Figure 2*. The intensity of these events could also reasonably be expected to increase with increasing PMMA content. As can be seen from our results, neither of these criteria is satisfied. Relaxations can, however, be observed at 40 and 50°C in $G'$ for PU-*g*-PMMA 30/12 000/25 and 30/12 000/50, respectively. In both these polymers this event is also seen as continuing rise, but with a smaller gradient, in tan $\delta$, after the $\delta$ event. In the d.s.c. experiments, these transitions were seen at 50 and 62°C for PU-*g*-PMMA 30/12 000/25 and 30/12 000/50, respectively. Thus, these results mirror the d.s.c. results and further confirm the conclusions in that work. That is, that PMMA in these materials exists in a homogeneous amorphous blend with some of the PCL and hard segment.

The hard-segment $T_g$ seen in the PU30 results can be observed in PU-*g*-PMMA 30/12 000/25 in both $G''$ and tan $\delta$, but is absent in PU-*g*-PMMA 30/12 000/50. $\alpha$ occurs in PU-*g*-PMMA 30/12 000/25 at 120°C in $G''$, as a continued decrease in $G'$ and as an increase above 100°C in tan $\delta$ which takes that parameter off-scale. These observations suggest that hard-segment domains are present in PU-*g*-PMMA 30/12 000/25, but are absent in PU-*g*-PMMA 30/12 000/50. That is, as the PMMA content of the polymer increases the degree of mixing between the hard segments and soft segments also increases. This result is then in good agreement with the increase in tan $\delta$, discussed previously, and with the d.s.c. data. In the d.s.c. data, no thermal events which could be assigned to $\alpha$ processes were observed in PU-*g*-PMMA 30/12 000/50, whereas a broad peak was observed in PU-*g*-PMMA 30/12 000/25 which covered a lower temperature range than in the linear polymer, PU30.

## *Conclusions*

In general, these results parallel the d.s.c. data[3] and confirm some of the conclusions in that work. That is, hard segment/soft segment phase separation of the PU backbone is decreased with soft-segment grafting, and all of the PMMA is mixed in with PCL.

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