The Formation and Properties of Acrylic-Polyurea Interpenetrating Networks Formed by Reaction Injection Moulding (RIM)

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SUMMARY: Interpenetrating networks (IPNs), comprising a crosslinked acrylic as one component and either a rubbery copoly(ether-urea) or a glassy copoly(urea-isocyanurate) as the other component, have been formed by reaction injection moulding (RIM). Reaction kinetics during RIM processing of the IPNs were studied using adiabatic temperature rise (ATR) measurements. The effects of (i) crosslinker concentration in the acrylic component and (ii) the weight fraction of acrylic, on the formation of the IPNs during RIM and on the dynamic mechanical properties of finally-formed IPNS, were evaluated. The results are interpreted in terms of differences in the rates of polymerisation and in the solubilities of the acrylic- and polyurea-forming components, and of the phase-separated structures of the IPNs.

Introduction

Previous studies on the formation of simultaneous IPNs, produced via RIM, have involved systems based on polyurethane/polyesters,[1)] polyurethane/epoxies[2)] and acrylic/polyurethanes.[3,4)] However, to date, there have been no systematic studies on RIM-IPNs based on either acrylic/copoly(ether-urea) (Ac/PUr) or acrylic/copoly(urea-isocyanurate) (Ac/co-PUrI) systems. Although polyurethanes are the most extensively studied RIM materials,[5)] RIM copolyurea materials[6-8)] have generated considerable interest in the past decade because of their superior thermal stability and hydrolysis resistance compared with polyurethanes. However, the very fast reaction rates characteristic of copolyurea-forming systems can give rise to processing problems although these may be overcome by the addition of a reactive diluent to decrease the concentration of the polyurea-forming reactants. A suitable reactive diluent not only reduces the reaction rate whilst maintaining the good mechanical properties characteristic of polyureas, but also provides an efficient route to the formation of IPNs: the

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RIM process is therefore particularly suitable for the formation of simultaneous *in situ* IPNs. The reactants for the two networks are mixed by impingement under high pressure and the two networks are formed via different polymerisation mechanisms within the same short time-scale. The simultaneous mixing and polymerisation processes produce extensive chain entanglements which increase connectivity and interaction between the IPN components and reduce the overall degree of phase separation.

This paper reports the results of studies on the processability of IPNs, designated Ac/PUr and Ac/co-PUrI, in terms of factors such as mixing efficiency and reaction kinetics which affect their formation via RIM. The results of *in situ* monitoring during RIM, via adiabatic temperature rise (ATR) measurements, and *a posteriori* characterisation using dynamic mechanical-thermal spectroscopy on the RIM IPN materials are reported.

Experimental Part

Reactants

The two series of IPNs studied, designated Ac/PUr and Ac/co-PUrI, are defined as follows, using general descriptions of the two polymer network components.

Ac/PUr: a glassy acrylic component and a rubbery poly(ether-urea) component;

Ac/co-PUrI: a glassy acrylic component and a glassy copoly(urea-isocyanurate) component.

In all IPNs, the crosslinked acrylic component was formed from methyl methacrylate and a dimethacrylate crosslinker using a redox initiator. The other components in the IPNs all contained the same rubbery soft-segment phase, a branched poly(ether-urea), formed from the same aromatic polyisocyanate and aliphatic diamine-functionalised polyether. In addition, the copoly(urea-isocyanurate) components in Ac/co-PUrI contained crosslinked polyisocyanurate hard-segment phases formed from a large stoichiometric excess of the aromatic polyisocyanate using a trimerisation catalyst.

The polyisocyanate used, VM021 (ex. ICI Polyurethanes), was a pre-polymer variant of 4,4'-diphenylmethane diisocyanate (MDI) and was a liquid reactant with an equivalent weight[†] E_n = 178 g mol^{-1}. The liquid diamine-functionalised polyoxypropylene was Jeffamine D2000 (ex. Texaco Chemical Company), with a nominal M_n-value of 2000 g mol^{-1} and an E_n-value[†] of 980 g mol^{-1}. The trimerisation catalyst, DABCO-TMR (ex. Air Products) was a quaternary

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[†]E_n is the molar mass per functional group, determined by end-group analysis.[9)]

ammonium carboxylate, N-hydroxypropyltrimethyl ammonium-2-ethylhexanoate. The methyl methacrylate, MMA (ex. Aldrich), was a technical grade product, and the crosslinker, Diacryl 121 (ex. Akzo), was bisphenol-A ethoxylate (2EO/phenol) dimethacrylate, with a nominal M_n-value of 540 g mol^{-1}. The initiator for the acrylic polymerisation was a redox system comprising benzoyl peroxide, BPO, (recrystallised from chloroform) and N,N-dimethyl-*p*-toluidine, DMPT.

IPN Materials Coding

The coding and composition of each IPN, formed by RIM, are shown in Table 1. Also given in the table are details of the materials variables used in the formation of the various IPNs, namely, (i) the degree of crosslinking in the acrylic component in Ac/PUr-1 to Ac/PUr-5 at constant Ac/PUr composition, and (ii) the relative proportions by weight of acrylic and copoly(urea-isocyanurate) components in Ac/co-PUrI-1 and Ac/co-PUrI-2, in which the degree of crosslinking in the Ac component and the proportions of soft-segment and hard-segment phases in the PUrI components are constant.

Table 1: Acrylic-polyurea IPNs formed by RIM. A summary of the materials variables and the partitioning of reactants, catalysts and initiator between the two reactant streams (A and B) used to prepare the IPNs, Ac/PUr and Ac/co-PUrI.

IPN [(a)]	**Materials Variable**	**RIM Reactant Stream Composition**	
		Stream A	**Stream B**
Ac/Pur[(b)] 1 to 5	Ac crosslink density: MMA/Diacryl 121 w/w %	polyisocyanate VM021 acrylate monomer MMA initiator BPO	polyether D2000 crosslinker Diacryl 121 catalyst DMPT
Ac/co-PUrI[(c)] 1 to 2	IPN composition: Ac/co-PUrI w/w %	polyisocyanate VM021 acrylate monomer MMA initiator BPO	polyether D2000 crosslinker Diacryl 121 catalyst DMPT and TMR

[(a)] In all IPNs, the Ac components were formed using the same initiator and catalyst contents of 1.0 and 0.33 % by weight of acrylic monomers, respectively.
[(b)] IPN composition constant: Ac/PUr = 43/57 w/w %.
[(c)] Ac crosslink density constant: MMA/Diacryl 121 = 31/69 w/w %.
PUrI composition constant: poly(etner-urea)/polyisocyanurate = 25/75 w/w %.

Reactive Processing of IPNs

IPNs were produced as rectangular plaques (76 x 140 x 3 mm) using laboratory-scale Micro-RIM equipment that has been described in detail elsewhere.[10] The various reactants and catalysts used for each IPN were carefully formulated between the two reactant streams

required for the RIM process, (see Table 1), so as to avoid any solidification and reaction in the storage tanks of the Micro-RIM equipment. The reactant streams were recycled several times, at high pressure prior to mould-filling, to ensure complete mixing and uniform temperature and viscosity of the reactants.

Adiabatic Temperature Rise (ATR) Measurements

ATR measurements were made using an insulated reactor in which one end of a short length of PVC tubing was connected to a nozzle mounted on the outlet of the mix-head on the Micro-RIM apparatus and the other end was positioned in a polypropylene cup. Two thermocouples were positioned in the cup and temperature-time data were recorded at a sampling rate of either 3 Hz or 5 Hz, depending on the rates of polymerisation operative during RIM, using a Macintosh II PC fitted with a Strawberry Tree ACM2-12-8 Data Acquisition board and a Workbench Software package. All ATR data were subjected to a heat-loss correction applied according to a global heat transfer coefficient derived from post-reaction cooling curves as described in detail elsewhere.[11)]

Dynamic Mechanical-Thermal Analysis (DMTA)

DMTA spectra of IPNs were obtained using a Polymer Laboratories Dynamic Mechanical Thermal Analyser (PL-DMTA). Specimens in the form of rectangular, double-cantilever beams (40 × 10 × 3 mm) were analysed in the temperature range −100 to 300 °C at a heating rate of 5 °C min^{-1} using a fixed frequency of 1 Hz. For each IPN, mean DMTA spectra comprising storage flexural modulus and loss tangent versus temperature plots were obtained from separate analyses of three specimens.

Results and Discussion

Processability and Evaluation of Mixing Quality

The two types of IPN (Ac/PUr and Ac/co-PUrI) displayed different processing characteristics and mixing qualities. Ideally, for the formation of each IPN component, the various reactants, initiators and catalysts required, which are partitioned between the two streams in the RIM equipment, must be mixed molecularly to facilitate uniform and complete polymerisation. The residence time and the degree of turbulence (Reynolds number) in the RIM mix-head affect the diffusion rate at which reactants for the two IPN components become molecularly mixed. Mixing quality, which depends on the diffusion rate, is determined by several factors including reactant viscosity and miscibility, and the intrinsic rates of polymerisation

associated with each component. In the latter case, the intrinsic difference in reaction rates between the free-radical chain polymerisation of the acrylate monomers and the step polyaddition forming the poly(ether-urea) or copoly(urea-isocyanurate) is critical. Half-times for isocyanate and aliphatic primary amine reactions are reported[11] to be of the order of 2×10^{-3} s, such that the formation of the poly(ether-urea) is extremely fast and is accompanied by rapid increases in molar mass and viscosity which limit diffusion rates.

Mixing quality in reactive processing is therefore very important, especially for the formation of simultaneous IPNs. Intensive mixing of the reactants and catalysts used to produce the IPNs is required to prevent macro-phase separation between components and to produce homogeneous materials. The reaction kinetics controlling the relative rates of polymerisation of the components in these types of RIM-IPNS, have significant effects on phase separation that occurs during the structure development of the materials. It is essential then to balance the competition between the kinetics of reaction and of thermodynamics, leading to gelation and vitrification, during the formation of the IPNs.

In the Ac/PUr IPNs, the rubbery branched poly(ether-urea) is formed almost instantly upon mixing but, despite its fast rate of polymerisation, remained dissolved in the acrylic monomers allowing diffusion and molecular mixing of the redox system within the polyurea phase. Efficient polymerisation of the acrylate monomers was therefore possible in the presence of the dissolved polyurea component, and the good mixing and high conversion achieved resulted in a uniform IPN structure, as imaged by optical microscopy.

In the Ac/co-PUrI, although the isocyanurate-modified polyurea and the acrylic components are both crosslinked, their rates of formation are slower than that of the poly(ether-urea) components in the Ac/PUr IPNs, again allowing longer times for all of the reactants and catalysts to mix more efficiently in the RIM mix-head and so enhance polymerisation conditions for both IPN components. The resulting IPN materials therefore possess more uniform morphological structures. The mixing characteristics and the effects on polymerisation kinetics are considered in more detail in terms of adiabatic temperature rise data in the next section.

Reaction Kinetics

Adiabatic temperature rise (ATR) measurements are widely-used to study the reaction kinetics in fast polymerisations because of the highly-exothermic character of polymerisations and the low thermal conductivities typical of polymer materials. The sequence of polymerisations and the relative reaction rates occurring during IPN formation can be

observed directly from ATR data. The effects of the different materials variables (see Table 1) on the reaction kinetics of the two types of IPN are discussed in the following two sections.

The effects on IPN formation of varying the degree of crosslinking in the acrylic component are shown by the ATR curves in Fig.l for IPNs Ac/PUr-1 to Ac/PUr-5 in which different percentage weight ratios of MMA:Diacryl 121 in the range 9:91 to 67:33, respectively, were used. The viscosity of MMA is significantly lower than that of Diacryl 121 (~0.001 and 0.89 Pa s, respectively, at 24 °C) so that as the weight ratio of MMA increases from Ac/PUr-1 to Ac/PUr-5, the initial viscosity of the IPN reactant mixture (in the RIM mix-head) decreases which increases mixing efficiency and enhances diffusion of reactants and catalysts. In addition, with increasing MMA content, the concentration of reactive double bonds [C=C] in the acrylate monomer mixture also increases. Both factors have an effect on the overall adiabatic temperature rise in these IPNs. The ATR curves in Fig. l have similar sigmoidal shapes consistent with the sequential *in situ* polymerisations forming the PUr and Ac components. The formation of the PUr component occurs rapidly in the presence of the acrylate monomers, which act as a diluent, and the magnitude of the initial temperature rise (at very short times) increases from Ac/PUr-1 to Ac/PUr-5 because of the decrease in viscosity of the initial IPN reactant mixture as the MMA content increases. Subsequent induction times of between 10 and 20 s were observed for polymerisation of the acrylate monomers, and gelation of the acrylic-forming components occurred between 20 and 35 s, approximately at the mid-points of the ATR curves where the maximum temperature rises are observed. The maximum adiabatic temperature rise, $\Delta T_{ad,max}$, increases from 115 to 140 °C as [C=C] increases from 2.03 to 3.01 mmol cm^{-3} along the series Ac/PUr-1 to Ac/PUr-5. However, the magnitude of $\Delta T_{ad,max}$ is less than that (~ 170 °C) observed for MMA/Diacryl 121 mixtures polymerised in isolation. Lower values of $\Delta T_{ad,max}$ in IPNs are observed because polymerisations forming the acrylic components occur in the presence of the rapidly-formed rubbery PUr component. Consequently, complete mixing of the acrylate monomers and catalysts is inhibited, and polymerisations which have to occur either within or surrounded by the PUr component, are limited by diffusion control.

In contrast to the Ac/PUr IPNs, the acrylic/copoly(urea-isocyanurate) IPNs are full-IPNs comprising two crosslinked networks, and both component polymers have relative slower reaction rates and need catalysts or initiators to effect efficient IPN formation. Temperature-time profiles for acrylic/copoly(urea-isocyanurate) IPNs comprising different weight proportions of Ac and co-PUrI components are shown in Fig. 2. Both profiles show two-stage

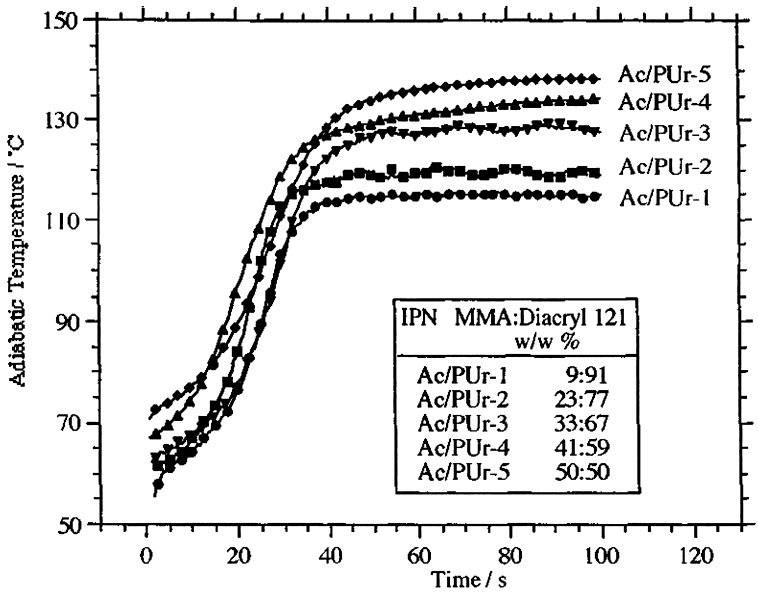

Fig. 1: Adiabatic temperature rise versus time profiles for Ac/PUr-1 to Ac/PUr-5 showing the effects of varying the weight ratio of MMA/Diacryl 121 at constant IPN composition.

polymerisation processes demonstrating clearly the formation of sequential IPNs. The Ac component is formed first and the relative adiabatic temperature rises associated with the formation of the Ac and co-PUrl components scale approximately with IPN composition. The polymerisation sequence in these Ac/co-PUrl IPNs cannot be changed, irrespective of the relative amounts of redox initiator and TMR catalyst used, with the trimerisation of isocyanate always following polymerisation of the aery late monomers. The rate of polymerisation and the adiabatic temperature rise, $\Delta T_{ad,Ac}$, associated with the polymerisation of the acrylate monomers are significantly greater the higher the ratio of Ac to co-PUrl in the IPNs. Consequently, as a result of the lower value of $\Delta T_{ad,Ac}$, a much longer induction time, 65 s for Ac/co-PUrI-2 compared to 40 s for Ac/co-PUrI-1, is required for the initiation of the trimerisation reaction of isocyanate groups to form the sequential co-PUrI network.

Comparison of the two types of IPNs, Ac/PUr-3 and Ac/co-PUrI-2, with similar contents of ~40 % by weight of Ac component, shows that the order in which polymerisations occur has a significant effect on the temperature-time profiles. For example, the induction times (20 cf. 55 s) and the times to "complete" reaction (60 cf. 120 s) involved in the formation of Ac components are approximately doubled in Ac/co-PUrI-2, due to the presence of the large

excess of unreacted MDI (required for polyisocyanate formation) which acts as a "heat sink" and absorbs the heat evolved by initial reaction of the acrylate monomers.

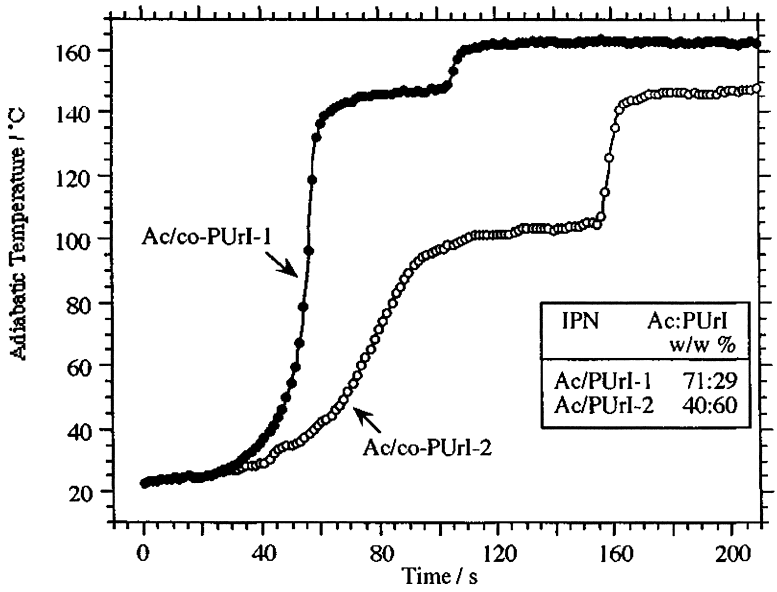

Fig. 2: Adiabatic temperature rise versus time profiles for Ac/co-PUrI-1 and Ac/co-PUrI-2 showing the effects of varying the weight ratio of Ac/PUrI at constant Ac and co-PUrI composition (as detailed in Table 1).

Dynamic Mechanical-Thermal Analysis (DMTA)

The DMTA spectra for the Ac/PUr IPNs in Fig. 3 show two well-defined transitions in terms of the peaks in tanδ and of the corresponding step changes in modulus, indicating that these IPNs are clearly two-phase materials. The transitions at the lower temperature around -20 °C, designated T_g^S are associated with the glass transition of the poly(ether-urea) component, and those at the higher temperature around 100 °C, designated T_g^{Ac}, are associated with the glass transition of the crosslinked acrylic component. Decreasing crosslinking in the Ac component, that is, increasing the percentage weight ratio MMA:Diacryl 121 from 9:91 to 50:50 along the series Ac/PUr-1 to Ac/PUr-5, has only a small effect on the location and intensity of the transition at T_g^S. In contrast, the transition at T_g^{Ac} shows a progressive increase in intensity as crosslink density decreases in the Ac component, consistent with the formation of a looser Ac network comprising chains with greater molecular mobility.

Although the IPNs possess a two-phase structure, there is some degree of chain interpenetration between the Ac and PUr components which varies with crosslinking in the Ac component. In the temperature region 0 to 80 °C, that is above T_g^S, but below T_g^{Ac}, the modulus at any temperature increases as the crosslink density decreases along the series Ac/PUr-1 to Ac/PUr-5, indicating a systematic increase in the degree of interpenetration between the Ac and PUr components in the IPNs. The rubbery modulus of the PUr component is increased by the reinforcing effect of the glassy Ac component, and the level of reinforcement increases with the degree of interpenetration.

The Ac/co-PUrI IPNs also possessed a two-phase morphology as shown by the DMTA spectra in Fig. 4. Again, there are two well-defined transitions in terms of the peaks in tanδ and of the corresponding step changes in modulus, and the relative tanδ peak intensities and step decreases in moduli for the transitions scale approximately with IPN composition. In contrast to the Ac/PUr IPNs in Fig. 3, however, the transitions at the lower temperature around 110 °C are associated, as before, with the glass transition of the crosslinked acrylic component (T_g^{Ac}), whereas those at the higher temperature around 165 °C are associated with the glass transition of the co-PUrI component. It should be noted that, in addition to the phase separation between Ac and co-PUrI components in these IPNs, the co-PUrI component also possesses a co-continuous microphase-separated structure[9,12] comprising poly(ether-urea) soft-segment and polyisocyanurate and hard-segement phases. The transition around 165 °C, designated T_g^H, is therefore associated with the glass transition of the polyisocyanurate-rich hard-segment phase: the glass transition associated with the poly(ether-urea) soft-segment phase, is only evident as small inflexions in the modulus curves over the temperature region -30 to 20 °C.

Comparison of the DMTA spectra for the two types of IPNs shows that, in terms of their applications as structural materials, the Ac/co-PUrl IPNs possess much superior mechanical properties around room temperature. This is particularly evident over the temperature range -30 to 80 °C where, for example, the modulus of ~ 10^9 Pa for Ac/co-PUrI IPNs changes only slightly with temperature whereas that for Ac/PUr IPNs decreases significantly by two orders of magnitude (~ $10^9$to 10^7 Pa). In addition, the decreases in mechanical properties at temperatures above T_g^{Ac}, are much less dramatic in Ac/co-PUrI IPNs, depending on composition, due to the presence of the highly crosslinked co-PUrl component.

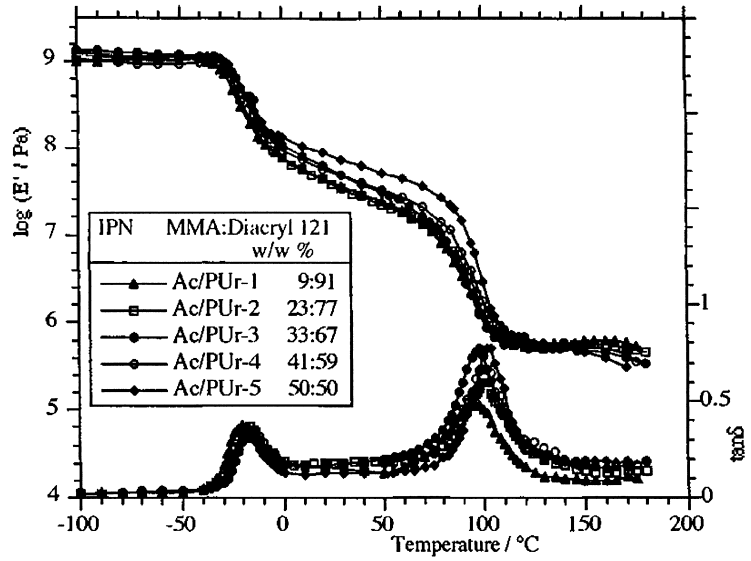

Fig. 3: Dynamic mechanical-thermal spectra showing plots of storage shear modulus (log E') and mechanical damping (tanδ) versus temperature for Ac/PUr-1 to Ac/PUr-5. Plots show the effects of varying the weight ratio of MMA/Diacryl 121 at constant IPN composition.

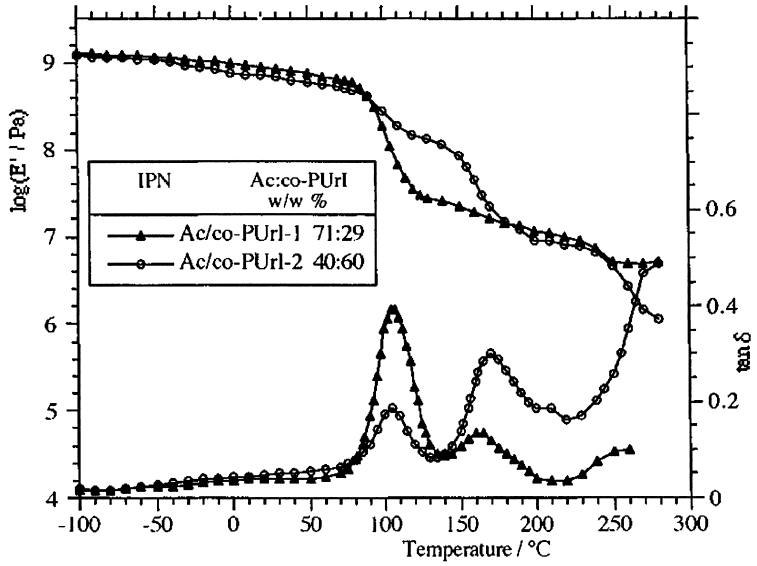

Fig. 4: Dynamic mechanical-thermal spectra showing plots of storage shear modulus (log E') and mechanical damping (tanδ) versus temperature for Ac/co-PUrI-1 and Ac/co-PUrI-2. Plots show the effects of varying the weight ratio of Ac/co-PUrI at constant Ac and co-PUrI composition (see Table 1).

Conclusions

Reaction injection moulding has enabled semi- and full-IPNs to be produced in short cycle times (< 3 minutes) from highly incompatible acrylic- and polyurea-forming systems via the different types of polymerisation, viz., chain and step. Rapid and efficient mixing of reactants, initiator and catalysts was provided by the high-pressure impingement mixing characteristic of the RIM process. Studies of the rapid reaction kinetics were readily obtained from adiabatic temperature rise measurements which clearly showed the sequential characteristics of both types of IPN formation producing materials with two-phase morphological structures. In Ac/PUr IPNs, the first-formed polymer was the rubbery poly(ether-urea) component whereas that in Ac/co-PUrI was the crosslinked acrylic component. Decreasing the degree of crosslinking in the Ac component in Ac/PUrI IPNs, by increasing the weight ratio of MMA:Diacryl 121, improved mixing efficiency during processing and resulted in more complete polymerisation of the Ac component. Consequently, a greater degree of chain interpenetration between Ac and PUr components in the Ac/PUr IPNs was achieved, as observed in DMTA spectra, which also confirmed the two-phase morphological structures of the IPNs. All of the IPNs showed two major glass transitions, with that at 110 °C associated with the Ac components, common to both types of IPN. Superior mechanical-thermal behaviour was observed for the Ac/co-PUrI IPNs, which showed a second glass transition at ~ 170 °C associated with the co-PUrI component, compared with Ac/PUr IPNs which showed a pronounced low temperature transition for the PUr component at ~ -20 °C.

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