

Mechanical and Morphological Study of Polyurethane/Polystyrene Interpenetrating Polymer Networks Containing Ionic Groups

DOUGLAS J. HOURSTON, FRANZ-ULRICH SCHÄFER,* NICHOLAS J. WALTER,[†] MICHAEL H. S. GRADWELL

Institute of Polymer Technology and Materials Engineering, Loughborough University, Loughborough, Leicestershire, LE11 3TU, United Kingdom

Received 15 March 1997; accepted 2 August 1997

ABSTRACT: The viscoelastic and mechanical properties and the morphology of polyurethane (PUR)/polystyrene (PS) interpenetrating polymer networks (IPNs) containing ionic groups have been investigated. Dynamic mechanical thermal analysis (DMTA) revealed a pronounced change in the viscoelastic properties upon the introduction of ionic groups. For the 70 : 30 and 60 : 40 PUR/PS IPN compositions, the DMTA data changed from a dominant PUR to a dominant PS loss factor peak. Higher intertransition loss factor values indicated a significant improvement of IPN component mixing with increasing ionic content. The stress at break values increased only moderately, whereas sharp rises in Young's modulus and hardness values were found at 2 wt % ionic groups. At the same time, the strain at break values decreased by half. Scanning and transmission electron microscopy (TEM) indicated a grossly phase-separated morphology for the 70 : 30 PUR/PS IPN without ionic groups. With increasing methacrylic acid (MAA) content, the PS phase domain sizes decreased. At 2 wt % of ionic groups, a TEM micrograph showed interconnected PS phase domains resembling a network structure.
© 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1973–1985, 1998

Key words: interpenetrating polymer networks; polyurethane; polystyrene; ionic groups; dynamic mechanical properties, morphology

INTRODUCTION

Interpenetrating polymer networks (IPNs) exhibiting various degrees of phase separation were prepared.^{1–3} In addition to the reaction kinetics, the miscibility of the constituent polymers is of crucial importance in determining the IPN morphology. With highly immiscible polymer pairs,

the thermodynamic driving forces are so powerful that phase separation occurs before the kinetic ramifications can prevent it. Polyurethane (PUR) and polystyrene (PS) are one such highly immiscible polymer pair because of the polar nature of the PUR compared with the essentially nonpolar PS and the pronounced difference in their solubility parameters (δ),⁴ 20.5 (J/cm³)^{1/2} for the PUR and 18.5 (J/cm³)^{1/2} for the PS. A lesser degree of phase separation in PUR/PS IPNs has been achieved by conducting the synthesis at low temperature^{5–8} and high pressure,^{9–11} and by synthesis in a common solvent.¹² Also, the introduction of internetwork grafting^{13–15} through the incorporation of difunctional monomers such as hydroxyethyl methacrylate, the introduction of urethane acrylate-type compatibilizers^{14,15} into one net-

Correspondence to: D. J. Hourston.

* Present address: BASF AG, D-67056 Ludwigshafen, Germany.

[†] Present address: Raychem Ltd., Swindon, Wiltshire, SN3 5HH, United Kingdom.

Contract grant sponsor: German Academic Exchange Service, Deutscher Akademischer Austauschdienst DAAD.

Journal of Applied Polymer Science, Vol. 67, 1973–1985 (1998)

© 1998 John Wiley & Sons, Inc.

CCC 0021-8995/98/121973-13

work, and the presence of oppositely charged groups,^{16–18} were successful in bringing about a more miscible morphology.

A great number of studies^{19–21} have been devoted to ionomers based on sulfonated PS, poly(phenylene oxide) and segmented PURs. Fewer studies¹⁶ have been reported in the literature with regard to the improvement in miscibility in polymer blends²² and IPNs^{16–18} by introducing oppositely charged groups into the polymer backbone. The most commonly used²³ anionic species contain either carboxylate or sulphonate groups. The former are typically prepared by copolymerization of acrylic or methacrylic acid (MAA) with some comonomer by free radical polymerization,¹⁶ whereas the latter are more commonly prepared by functionalization of a preformed polymer.²⁴ Because of the simultaneous one-shot polymerization route for the PUR/PS IPNs, only the incorporation of potentially charged groups by copolymerization was practical in this study. The ionomer properties are influenced²¹ by various factors, notably ion content, type and position of ionic group, type of polymer backbone, and type of counter ion. Most commonly inorganic cations such as alkali and transition metals are used as counter ions. In this study, an organic molecule, a tertiary amine that incorporated into the PUR network, was selected for neutralization of the MAA. The aims of this study were to investigate the viscoelastic and morphological changes that took place when introducing ionic groups into the PUR/PS IPN. Furthermore, we attempted to use ionic interactions to control IPN miscibility in order to obtain a semi-miscible morphology that resulted in a material with high damping characteristics over a wide temperature range. The morphology was determined by a combination of transmission and scanning electron microscopy (TEM and SEM, respectively). Dynamic mechanical thermal analysis (DMTA) was used to determine the miscibility and the damping characteristics, while tensile testing and hardness measurements determined the mechanical properties.

EXPERIMENTAL

Materials

The PUR component hard segment was composed of 1,1,3,3-tetramethylxylene diisocyanate (TMXDI, kindly donated by Cytec, UK) and the crosslinker trimethylol propane (TMP, Aldrich, UK). The soft

segment was made up of polyoxypropylene glycol units of 1025 molar mass (PPG1025, BDH, UK). Stannous octoate (SnOc, Aldrich, UK) was used as the PUR catalyst. Styrene monomer (S, Aldrich, UK) was crosslinked with divinylbenzene (DVB, Aldrich, UK) and initiated with azoisobutyronitrile (AIBN, BDH, UK). *N*-methyl-diethanolamine (MDEA, Aldrich, UK) and MAA (Aldrich, UK) were incorporated into the PUR and the PS, respectively, as the potentially oppositely charged ionic sites.

IPN Preparation

The IPN preparation was described in an earlier publication.²⁵ In brief, the TMP was dissolved in the PPG1025 at 60°C; and at room temperature, the polymer component mixture including the S, DVB, and dissolved AIBN was added. Upon addition of the SnOc and the TMXDI, the components were stirred under nitrogen for 5 min. After degassing for 1 min at high vacuum, the mixture was cast in stainless-steel spring-loaded O-ring molds, which had been pretreated with CIL Release 1711 E release agent. The curing cycle consisted of three stages: 24 h at 60°C, 24 h at 80°C, and 24 h at 90°C.

For the IPNs with ionic groups, the same preparation method was used. The MDEA was added to the TMP and PPG1025, whereas the MAA was combined with the S, DVB, and AIBN. Incorporation of the agents was conducted at 0.5, 1, 2, 2.5, and 3 MAA wt % levels. The MAA weight percentages were taken with respect to the total component weight and the equivalent moles of MDEA added to result in a ratio of potentially oppositely charged groups of 1 : 1. All samples were stored in a vacuum oven at room temperature for at least 2 wk prior to use.

IPN Characterization

DMTA measurements were performed with a Polymer Laboratories MK II Dynamic Mechanical Thermal Analyzer. The samples were measured in the bending mode (single cantilever) at a fixed frequency of 10 Hz from –60 to 200°C using a heating ramp of 3°C/min. The 3-mm-thick test specimens were cut to a rectangular shape with 50 × 10 mm dimensions. The applied strain setting was ×4.

Stress–strain analyses were conducted at a crosshead speed of 50 mm/min using a JJ Lloyd 1 2000R tensometer equipped with a 500 N load

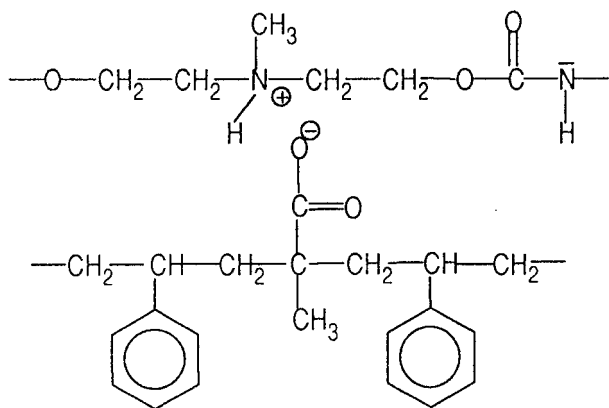


Figure 1 Interaction of tertiary amine (MDEA) and pendent carboxylic acid groups (MAA).

cell. Small dumbbells with a gauge length of 30 mm were used. Tests were conducted at $23 \pm 1^\circ\text{C}$ and the values quoted are an average of four or five samples.

Shore A hardness was determined using a Zwick model 3114 instrument, whereas Shore hardness D was measured using a Jamaica Instruments gauge. The testing was conducted at room temperature ($23 \pm 1^\circ\text{C}$). Hardness values quoted are an average of eight readings taken at random over the entire specimen surface.

TEM was conducted for a morphological investigation of the IPNs. The elastomeric samples were embedded into Spurr's epoxy resin²⁶ and ultramicrotomed with an LKA Bromma 8800 Ultratome III. Osmium tetroxide-stained and unstained samples were investigated. Staining of the 100-nm-thick sections was conducted in a 2% osmium tetroxide solution for 48 h, following the method of Kato.²⁷ The electron micrographs were taken with a Jeol Jem 100 CX instrument using an accelerating voltage of 60 kV.

SEM was conducted with a Leica Cambridge Stereoscan S360 instrument. The fracture surfaces were obtained from the broken tensile test specimens. These surfaces were sputtered with gold to avoid electrostatic charge and to improve image resolution.

RESULTS AND DISCUSSION

The success of improving IPN miscibility through ionic interactions depended on the transfer of the carboxylic acid proton to an amine base to result in the formation of an ion pair. The schematic interaction between MAA and MDEA is shown in Figure 1. Values for the acidity constant (K_a or

pK_a) were not readily available for MDEA and MAA. Also, these pK_a values are determined²⁸ in water and it is known²¹ that aqueous pK_a values could have been at best indicative, since acidities determined in aqueous media cannot be extrapolated with certainty to organic media. Thus a preliminary experimental study was undertaken in order to ascertain that this neutralization reaction occurred. Equimolar amounts of MDEA and MAA were weighed into a glass bottle and intimately mixed at room temperature. An immediate strong exothermic reaction indicated that proton transfer was achieved; 5 min after the initial mixing the glass bottle had cooled to room temperature, indicating that the neutralization reaction was complete. Thus it was decided that no change to the standard preparation procedure was necessary for the IPNs with ionic groups.

Viscoelastic Properties

DMTA studies of polymer blends and ionomers can be used to characterize indirectly their microstructure, to establish structure–property relationships, and to determine their damping characteristics. The formation of an ionomer results²³ in three important changes in the viscoelastic properties of a polymeric material. First, the glass transition temperature (T_g) generally increases with increasing ionization as a result of the reduced polymer backbone mobility due to the formation of ionic crosslinks. Second, an extended rubbery plateau modulus above T_g is observed, again because of the ionic network. Third, a high-temperature mechanical loss peak is observed above T_g , which is due to motion in the ion-rich phase. Thus miscibility and damping characteristics of the ionic IPNs were investigated by DMTA.

The PUR component was selected to predominate in this series of IPNs, since the overall objective of this research was to develop materials exhibiting high damping characteristics over a broad temperature range. See Hourston and Schäfer¹⁴ for details of the dynamic properties of the pure PUR. Therefore, the 70 : 30 and the 60 : 40 PUR/PS IPN compositions were studied. At 3 wt % in the 70 : 30 PUR/PS IPN composition, the highest MAA incorporation corresponded to 12 mol % MAA in the P(S-MAA) network. The loss-factor-versus-temperature data for the 60 : 40 PUR/PS IPN composition at various MAA weight percentages and MDEA equivalents are shown in Figure 2. With increasing ionic group content, a number of significant changes in the loss factor

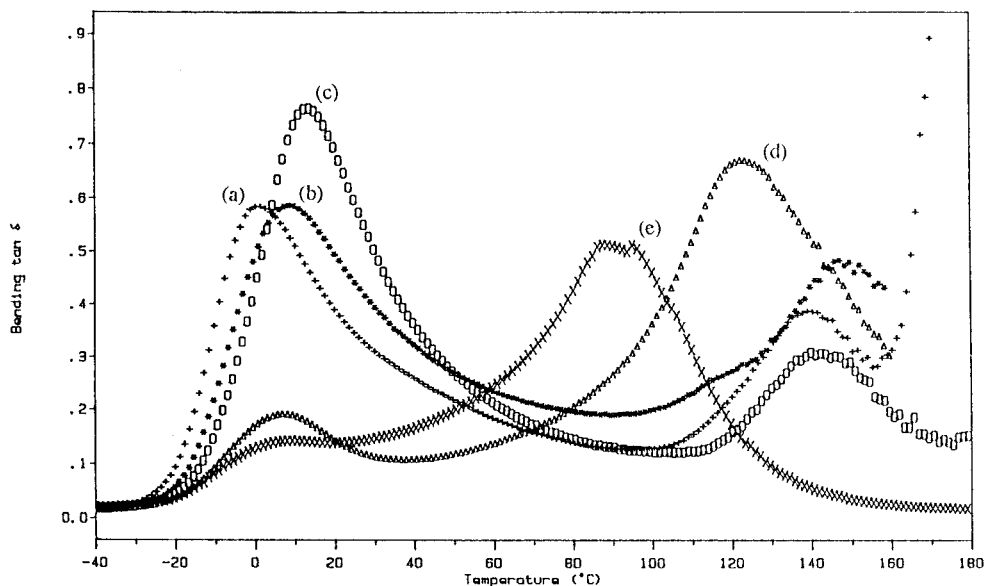


Figure 2 Loss factor versus temperature data for the 60 : 40 PUR/PS IPN at various levels of MAA weight percentages and MDEA equivalents: (a) 0% ionic groups, (b) 0.5%, (c) 1%, (d) 2%, and (e) 3%.

profile were observed. The loss-factor data for 0 and 0.5 wt % ionic groups were very similar [Fig. 2(a,b)]. At 1% incorporation [Fig. 2(c)], the PUR transition shifted to a slightly higher temperature (11°C) and increased in height, whereas the PS transition decreased slightly in height. At 2% incorporation of ionic groups [Fig. 2(d)], a dramatic change in the loss factor profile took place. The PUR transition, while still being roughly at the same temperature (6°C), decreased by a factor of 4 to a loss factor of 0.19, compared with 0.80 for the IPN with 1% ionic groups. The PS transition, on the other hand, shifted to a lower temperature (120°C) and increased considerably in size (0.68). At a level of 3% ionic groups [Fig. 2(e)], the PUR transition remained at the same temperature (6°C) and decreased slightly in size to 0.13. No longer were two transition peaks observed, but the PUR transition figured as a shoulder to the PS transition. The latter decreased further in size to 0.50 and shifted lower to 89°C. The fact that a pronounced PUR shoulder was still present at a 3% incorporation of ionic groups could be explained by the site of the ionic interactions in the PUR. The tertiary amine group was incorporated into the PUR hard segment. Thus the interactions that were introduced by the MAA mainly increased the miscibility of the P(S-MAA) with the PUR hard segment. This could explain why part of the PUR soft segment transition still remained

at a low temperature while a strong shift of the entire PS transition to lower temperatures was observed.

Two types of structure of ionomers have been reported.²⁹ Ionic aggregates termed "multiplets" consist of small numbers of associated ion-pairs that are dispersed in a low-polarity matrix. If the multiplets are close enough together for these regions of restricted mobility to overlap, larger regions of restricted mobility are formed. When such a region is large enough to exhibit its own T_g and behaves as a separate phase, it is termed a "cluster."²⁰ Since the latter phenomenon is observed at higher temperatures, one DMTA experiment was run up to 230°C. Figure 3 shows the loss factor, storage modulus, and loss-modulus data versus temperature for the 60 : 40 PUR/PS IPN at 3% incorporation of ionic groups. The storage moduli decreased in a two-step drop, up to a temperature of 120°C. At temperatures higher than 120°C, an increase in the storage moduli was observed. For the 60 : 40 PUR/PS IPNs without ionic groups the storage moduli decreased considerably at 180°C because of a softening of the dual network system. However, for the 60 : 40 PUR/PS IPN with 3% ionic groups, values for E' were still very high (13 MPa) at 180°C and continued to increase up to a temperature of 185°C. The extended rubbery plateau modulus is generally believed¹⁹ to result from the oppositely charged ionic

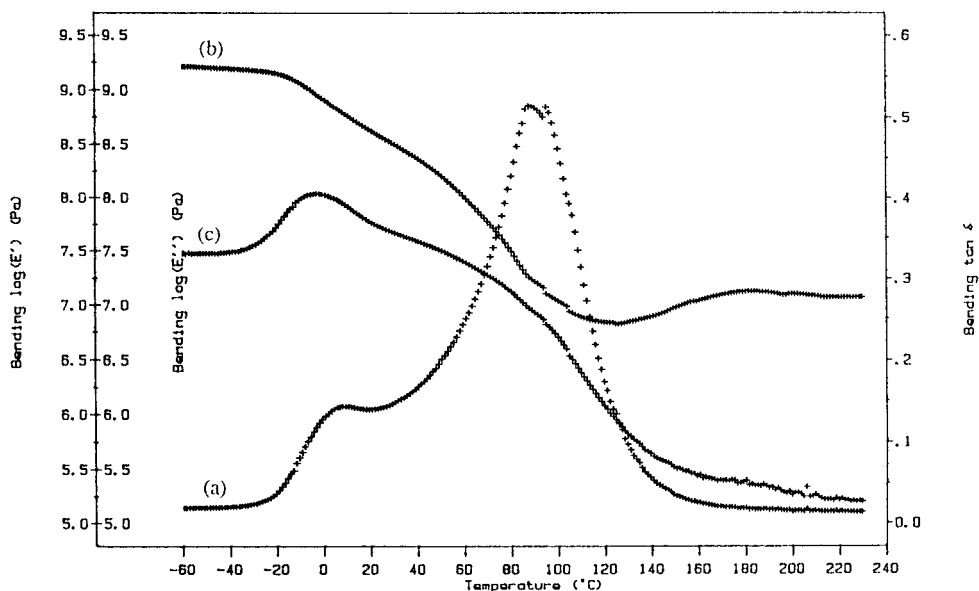


Figure 3 (a) Loss factor, (b) storage modulus, and (c) loss modulus versus temperature data for the 60 : 40 PUR/PS IPN at 3% MAA weight percentages and MDEA equivalents.

groups acting as additional crosslinks. The fact that the storage modulus not only exhibited an extended plateau but even increased could be explained as follows. In general, a significant increase in storage modulus can be caused³⁰ by the occurrence of a chemical reaction (i.e., crosslinking) or by the formation of crystalline domains. In this study, the increase in E' must have been caused by the formation of additional ionic crosslinks. At higher temperatures, a higher degree of chain segment mobility was obtained in the IPN. Carboxylic acid groups of the P(S-MAA) network that had not been neutralized or linked to quaternized amine structures came into contact with amine groups in the PUR network. As a result of the formation of additional crosslinks by the neutralization reaction, the storage modulus increased. At 185°C, a slight decrease in E' was observed which might have been associated with the breakdown of some ionic crosslinks. Viscoelastic measurements on ionomers have shown¹⁹ the existence of a high temperature loss peak between 200 and 240°C, which has been termed the "ionic cluster transition." This glass transition of the clustered material has been interpreted by most researchers as ion hopping,²⁰ a process by which the ion pairs migrate from one multiplet to another. The loss moduli versus temperature showed that this high temperature loss peak was not present up to a temperature of 230°C [Fig.

3(c)]. These PUR/PS IPNs could not be studied at higher temperatures because of the onset of PUR degradation which started to take place at 220°C.³¹

A considerable broadening and compatibilizing effect was achieved by the incorporation of 3% ionic groups into the 60 : 40 PUR/PS IPN. However, the transition height at the low-temperature end had severely decreased. In order to increase the height of the PUR soft-segment transition, the 70 : 30 PUR/PS IPN composition was chosen for the incorporation of ionic groups. Again, a very similar transition profile resulted from the 0 and 1% incorporation of ionic groups [Fig. 4(a,b)]. At 2% incorporation [Fig. 4(c)], the transition shape changed considerably in that the PS transition became predominant. Similarly to the 60 : 40 PUR/PS IPNs, the PUR transition decreased from a loss factor value of 0.81 (1% ionic groups) to 0.24 while remaining at roughly the same temperature (8°C). The PS transition, on the other hand, shifted to a lower temperature (106°C) and increased from 0.41 (1% ionic groups) to 0.48. A further increase in ionic groups (2.5 and 3%) provoked a further increase in PS loss factor height (0.53 and 0.55, respectively) and a shift to lower temperatures (94 and 78°C) of the PS T_g . With increasing incorporation of ionic groups, the PUR low-temperature transition decreased further. At 3% ionic groups, it was present only as a shoulder.

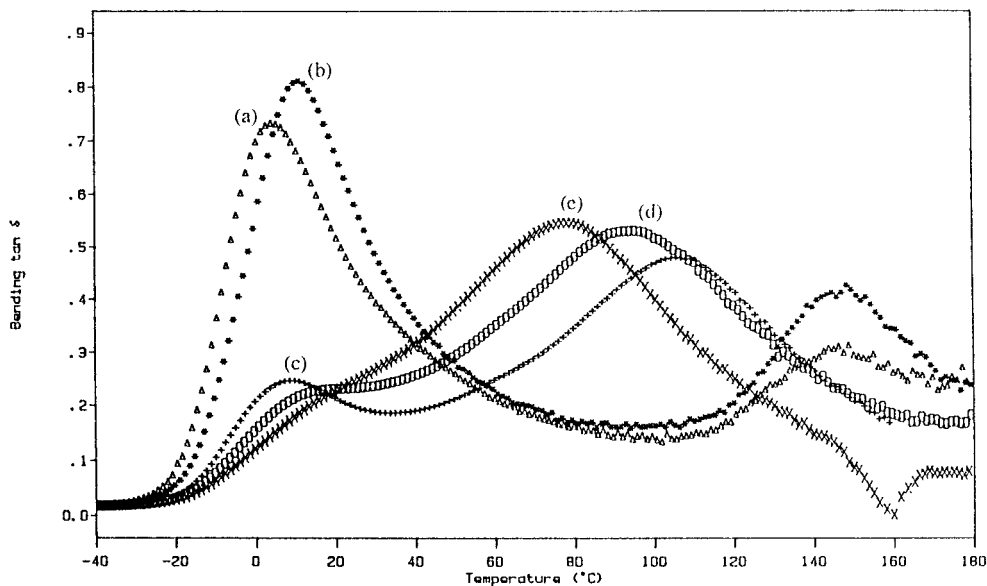


Figure 4 Loss factor versus temperature data for the 70 : 30 PUR/PS IPN at various levels of MAA weight percentages and MDEA equivalents: (a) 0% ionic groups, (b) 1%, (c) 2%, (d) 2.5%, and (e) 3%.

The latter indicated a pronounced increase in miscibility between the IPN components. The storage moduli of these 70 : 30 PUR/PS IPNs reflected the trends of the loss factor data (Fig. 5). The storage moduli of the IPNs with 2, 2.5, and 3% incorporation of ionic groups decreased in a

roughly linear pattern, which indicated a high degree of component mixing in these IPNs.

The increase in component mixing observed in these IPNs with ionic groups must have been brought about by specific intermolecular interactions between the PUR and the PS networks.

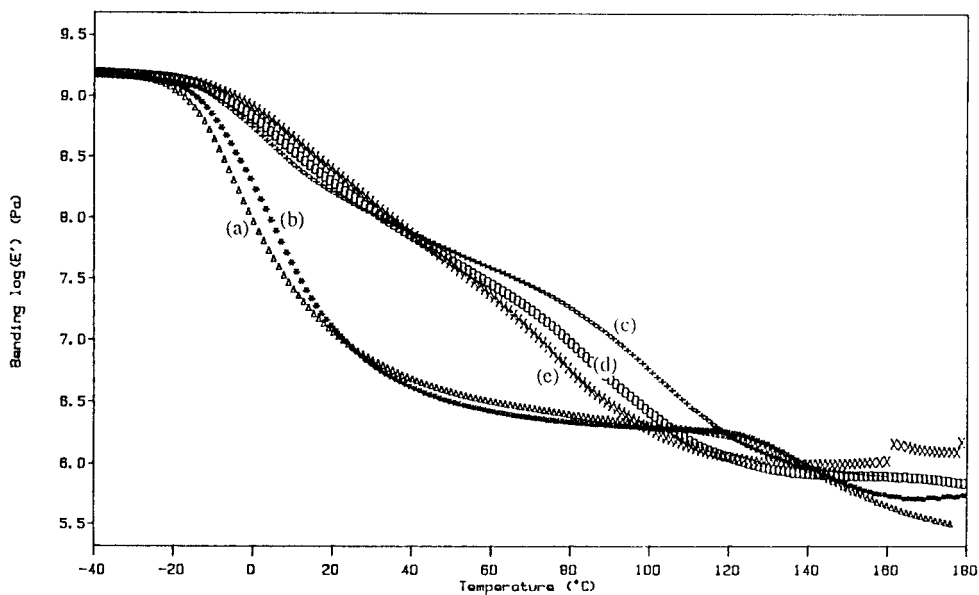


Figure 5 Storage moduli versus temperature data for the 70 : 30 PUR/PS IPN at various levels of MAA weight percentages and MDEA equivalents: (a) 0% ionic groups, (b) 1%, (c) 2%, (d) 2.5%, and (e) 3%.

Through the copolymerization of MAA with S, and the incorporation of MDEA into the PUR, there were three kinds of interactions possible between the two network polymers. The carboxylic acid groups of MAA could form hydrogen bonds with the urethane link. If neutralization occurred, ionic interactions were possible between carboxylate anions and quaternized amine moieties in the PUR. The introduction of internetwork grafting might have been a third mechanism for the MAA to improve PUR-PS phase mixing. Under certain conditions, isocyanates react³² with carboxylic acid groups to result in the formation of CO₂ and an amide. However, the carboxyl group of the MAA was unlikely to react with the forming PUR because its reaction rate with the NCO is much slower³² than that of the primary hydroxyl groups. Also, because of the low curing temperatures (maximum 90°C) and the low reactivity of the tertiary NCO groups of the TMXDI, no amide formation was believed to have taken place. It was of interest to ascertain whether the increase in miscibility was brought about by the formation of ion pairs or whether hydrogen bonding introduced by the MAA moieties in the PS alone was sufficient to achieve compatibilization. Therefore, a 60 : 40 PUR/PS IPN with 3 wt % MAA and no MDEA was prepared. The corresponding 60 : 40 PUR/PS IPN without MAA, but with the stoichiometric amount corresponding to 3 wt % MAA of MDEA was also prepared. These latter two were compared with the 60 : 40 PUR/PS IPN with 3% ionic groups and to that without ionic groups, respectively. The data on loss factor and storage modulus versus temperature for these four IPNs are shown in Figures 6 and 7. Very similar DMTA data were observed for the 60 : 40 PUR/PS IPNs with 3% ionic groups and for that with the 3% MAA alone. The loss factor transition heights in both IPNs [Fig. 6(b,c)] were virtually the same with 0.13 and 0.52 for the PUR and the PS, respectively. The T_g locations of the IPN with 3% MAA incorporation were at -4°C and 100°C for the PUR and the PS, respectively. The 3% ionic groups exhibited a slightly more component-mixed morphology with transitions at 6°C and 90°C for the PUR and the PS, respectively. The storage moduli versus temperature of both IPNs were also very similar [Fig. 7(b,c)]. Both IPNs had increasing moduli at temperatures higher than 120°C. The similar DMTA data indicated that no tertiary amine was necessary to neutralize the carboxylic acid group of the MAA in order to bring about an increase in miscibility in the

PUR/PS IPN. These results can be explained in two possible ways. First, no neutralization of the carboxylic acid occurred and the increase in miscibility was brought about by hydrogen bonding with the urethane link alone, as was suggested by Xiao and coworkers³³ when investigating PUR/P(MMA-MAA) IPNs. They suggested that a decrease in phase separation in PUR/P(MMA-MAA) IPNs was brought about by additional hydrogen bonding between the carboxyl groups and the urethane links in the PUR.³³ A second possibility was that neutralization of the carboxylic acid group took place involving the nitrogen in the urethane link. From the results in this study, the latter was much more likely. The extension of the rubbery plateau modulus to higher temperatures and the increase of the latter at temperatures higher than 120°C can be explained only by strong ionic interactions. Hydrogen bonding generally becomes³⁴ very weak at temperatures higher than 80°C. Some studies³⁵⁻³⁷ have suggested that urethane nitrogens in PUR chains are capable of undergoing quaternization. In a recent study investigating PUR/PS ionomer blends, Nantsohn and coworkers³⁵ found that the labile protons of sulfonic acid groups were preferentially transferred to allophanates, followed by urethane nitrogens and finally by tertiary amine nitrogens. Thus the latter explained the efficiency of 3% MAA incorporation in bringing about an increase in IPN miscibility. A neutralization reaction between the MAA and the nitrogen in the urethane link must have taken place. However, when both MAA and MDEA were present in the initial mixture, as in the preparation procedure in this study, the proton transfer was believed to have occurred mainly with the MDEA because during the initial mixing only very few urethane links had formed. The efficiency of MAA in increasing IPN miscibility might be a function of the incorporation level and, furthermore, of the degree of MAA neutralization. The extent of proton transfer from the MAA to the MDEA or urethane nitrogens could be a function of its acid strength and the basicity of the nitrogens. In this study, the extent of proton transfer was difficult to quantify other than from the increase in miscibility in the DMTA data. Fan and Bazuin²¹ recently attempted to make a quantitative calculation of the extent of proton transfer. Investigating tertiary amines of different basicity, they related the area under the absorption band at 900-906 cm⁻¹ to the degree of neutralization of the ionic groups.

Another interesting result was obtained when

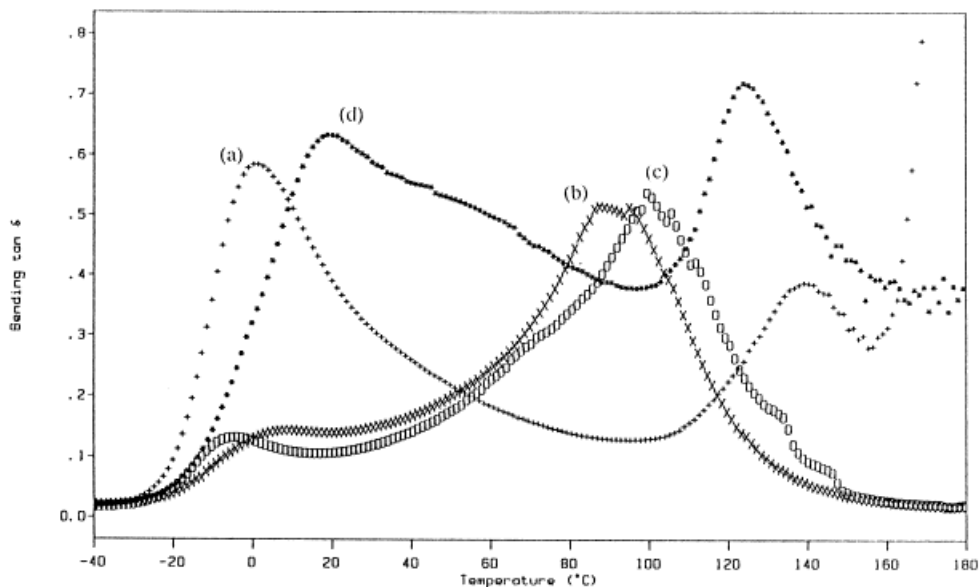


Figure 6 Loss factor versus temperature data for the 60 : 40 PUR/PS IPN at various levels of MAA weight percentages and MDEA equivalents: (a) 0% ionic groups, (b) 3% MAA and equivalent MDEA, (c) 3% MAA, and (d) MDEA equivalent to 3% MAA.

comparing the DMTA data of the unmodified 60 : 40 PUR/PS IPN with the respective counterpart containing 3 wt % MAA equivalent of MDEA. The loss-factor-versus-temperature data showed an inward shift of the PUR and the PS transition for the IPN containing the MDEA moieties. The PUR transition shifted from 1°C to 19°C while the PS

T_g shifted from 140°C to 122°C. More importantly, the PUR transition was extremely broad and exhibited high loss factor values up to a temperature of 100°C. As a consequence, the intertransition values were extremely high, with a lowest value of 0.38 compared with a value of 0.13 for the unmodified 60 : 40 PUR/PS IPN. The storage moduli

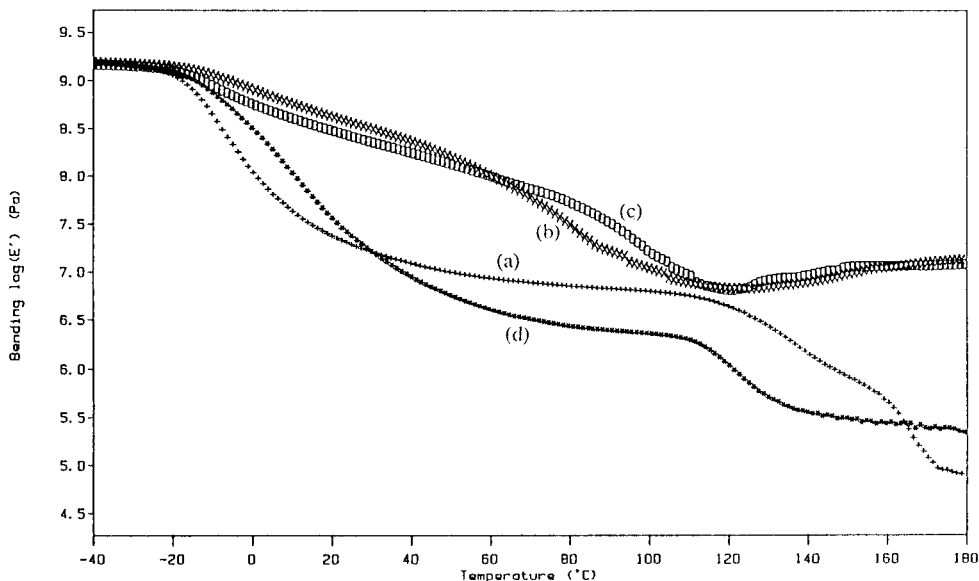


Figure 7 Storage moduli versus temperature for the 60 : 40 PUR/PS IPN at various levels of MAA weight percentages and MDEA equivalents: (a) 0% ionic groups, (b) 3% MAA and equivalent MDEA, (c) 3% MAA, and (d) MDEA equivalent to 3% MAA.

Table I Mechanical Properties for 70 : 30 PUR/PS IPNs with Different Levels of Oppositely Charged Groups

PUR/PS IPN MAA Level (wt %)	Stress at Break (MPa)	Tensile Properties			Hardness Shore	
		Strain at Break (%)	Young's Modulus (MPa)	Toughness [J]	A	D
0	12	770	4	14	59	35
1	13	330	4	7	67	44
2	14	370	85	12	92	61
2.5	14	360	82	13	93	61
3	14	330	89	10	94	61

exhibited a two-step drop mechanism indicating a phase-separated morphology for both IPNs [Fig. 7(a,d)]. The storage moduli at the PUR transition decreased more gradually and over a broader temperature range for the MDEA-containing IPN. This reflected the broader PUR loss factor transition. The pronounced difference between the two IPNs could not be explained with certainty and further study is needed. The fact that MDEA as a tertiary amine is also a strong catalyst for the PUR reaction might have played some role. Tin-based catalysts such as SnOc used in combination with tertiary amines are known³⁸ to exhibit a synergistic effect. Thus the resulting increase in reaction rate of the PUR network might have led to a faster buildup of a highly viscous reaction mixture which is known³ to restrict phase separation. The fact that tertiary amines are known³⁹ to favor the reaction of isocyanates with water was not believed to have had any influence because great care was taken to exclude humidity. The IPN with MDEA had very high damping characteristics with loss factor values of higher than 0.3 starting at 0°C up to the high end of the DMTA experiment (180°C). At 180°C, however, the mechanical properties were poor, which was manifested in a low storage moduli of 0.3 MPa.

Stress–Strain and Hardness Measurements

Miscible and semimiscible polymer blends often present advantages over immiscible blends.⁴⁰ Thus the mechanical properties of the 70 : 30 PUR/PS IPNs with improved miscibility through the incorporation of oppositely charged groups were investigated by tensile testing and Shore A and D hardness measurements. The stress and elongation at break, Young's modulus, the toughness index, and values for Shore A and D hardness are given in Table I. The values for the stress at

break increased with increasing content of ionic groups; however, the increase was not very significant. The unmodified 70 : 30 PUR/PS had a value for the stress at break of 12 MPa, whereas the corresponding IPN with 3% ionic groups exhibited a value (14 MPa) which was higher by 17%. The values for the strain at break showed a significant decrease with higher ionic group contents. They fell by more than half from the unmodified (770%) to the IPN containing 3% ionic groups (330%). Since the values for the toughness index are a function of the stress and the strain at break, the former were also lower for the IPNs containing ionic groups. The fact that the toughness index values were not as low as expected for the IPNs with 2, 2.5, and 3% ionic groups was because the shape of the stress–strain curve had changed. For the 70 : 30 PUR/PS IPNs with 0 and 1% ionic groups, high tensile stress values were obtained only at high elongations. The IPNs with 2, 2.5, and 3% ionic groups had high tensile stress values right from the start. As a consequence, relatively high areas under the stress–strain curve were obtained for the latter despite their low values for the strain at break. The important change in IPN properties that was observed from the DMTA data between the 1% and 2% incorporation of ionic groups was even more pronounced in the Young's moduli. The latter increased from low values of 4 MPa for 0 and 1% ionic group incorporation by a factor of more than 20 to 85, 83, and 89 MPa for the IPNs with 2, 2.5, and 3% ionic groups, respectively. The hardness values also reflected the dramatic change in the properties of the IPNs (Table I). This dramatic increase in modulus was believed to have resulted from a change in IPN morphology. The only explanation possible was that the glassy PS network must have assumed some degree of continuity at 2% ionic group incor-

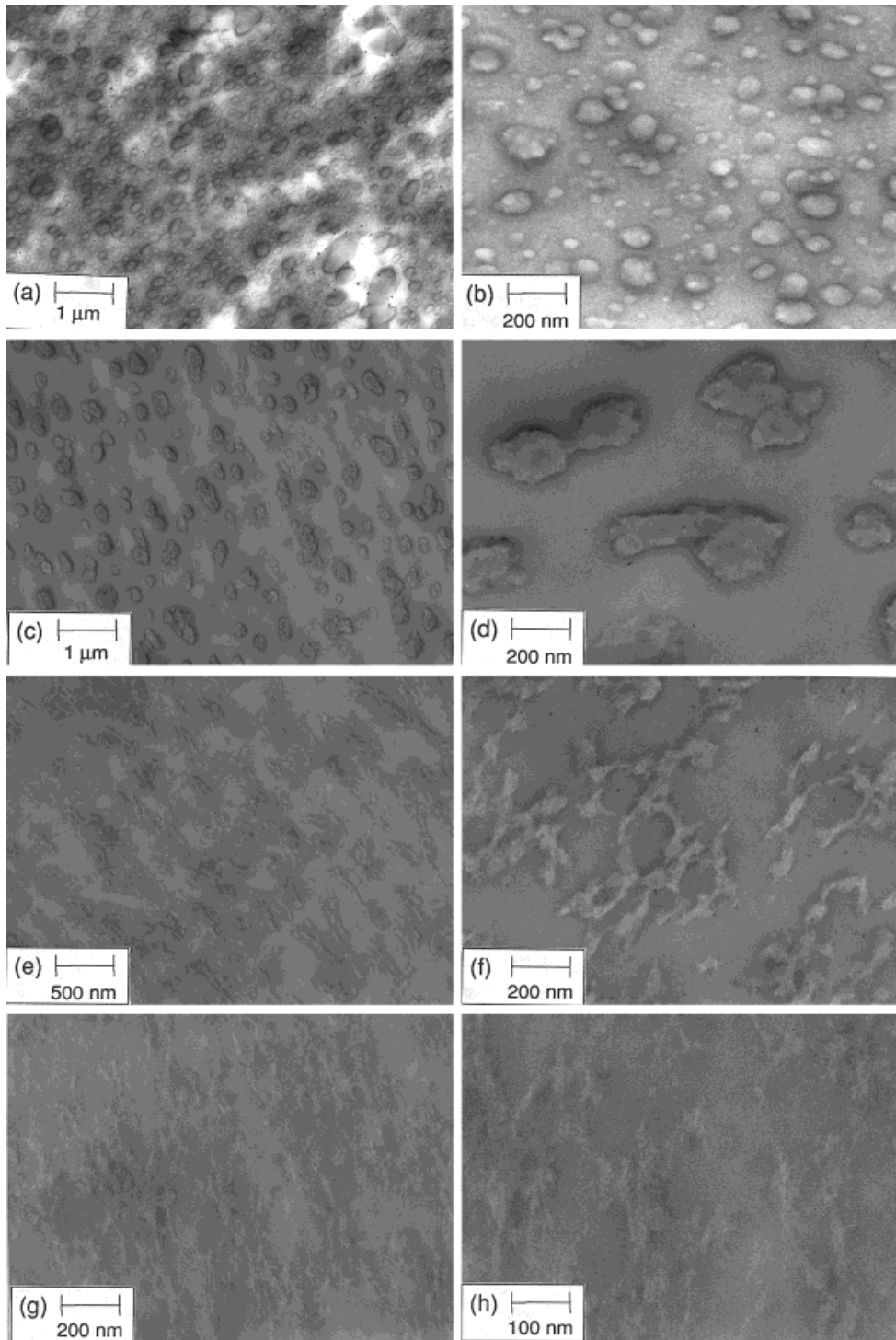


Figure 8 TEM micrographs for the 70 : 30 PUR/PS IPNs with different levels of oppositely charged groups. (a,b) 0% ionic groups; (c,d) 1%; (e, f) 2%; (g,h) 3%.

poration. In order to confirm this assumption, the morphology of these 70 : 30 PUR/PS IPNs with different ionic group contents were investigated by TEM and SEM.

Morphology by TEM and SEM

The findings made from DMTA and tensile testing for the 70 : 30 PUR/PS IPN composition with vari-

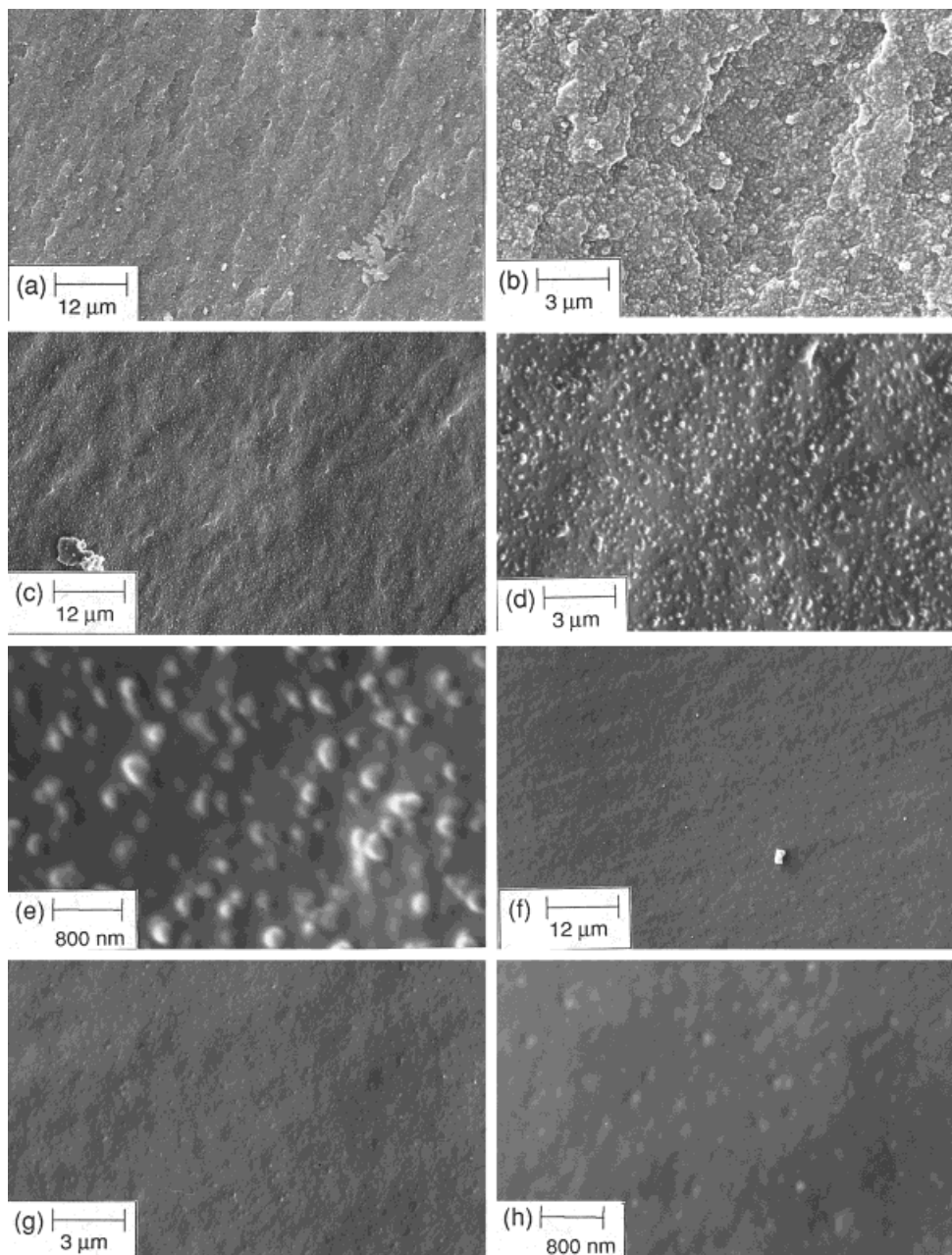


Figure 9 SEM micrographs for the 70 : 30 PUR/PS IPNs with different levels of oppositely charged groups. (a,b) 0% ionic groups; (c–e) 1%; (f–h) 2%.

ous levels of oppositely charged groups were confirmed by electron microscopy. The TEM micrographs showed significant changes in the IPN morphology (Fig. 8). The unmodified 70 : 30 PUR/PS IPN showed white spherical and ellipsoidal PS domains in a dark, osmium tetroxide stained, and predominantly PUR-containing matrix [Fig. 8(a,b)]. The PS domain sizes ranged in the order of 50 to 200 nm. The dark shell surrounding the PS domains is believed^{41,42} to have had a higher

PUR content than the matrix. At 1% ionic group incorporation [Fig. 8(c)], the PS phase domain sizes were clearly bigger (100 to 300 nm) than in the 70 : 30 PUR/PS IPN without ionic groups. Also, significantly fewer PS domains were noted and their shape was more irregular [Fig. 8(c)]. At a higher magnification, it was observed that two or three PS domains had joined to form these bigger aggregates [Fig. 8(d)]. At 2% ionic group incorporation, a substantial change in IPN mor-

phology occurred. The PS phase domains became smaller and formed an interconnected network [Fig. 8(e,f)]. The fact that the PS network assumed some degree of continuity at this incorporation level explained the findings from the DMTA data, tensile testing, and hardness measurements. At a 2% incorporation of ionic groups, the PS loss factor transition was higher than that of the PUR, indicating some degree of phase continuity of PS. Also, the Young's modulus and hardness values increased considerably. At 3% ionic groups, the PS phase structure was even finer and the network exhibited a higher degree of continuity [Fig. 8(g,h)].

The SEM micrographs confirmed to some extent the findings from TEM. Again, it was observed that the phase size generally decreased with increasing ionic group content (Fig. 9). Comparing the unmodified [Fig. 9(a,b)] 70 : 30 PUR/PS IPN with that containing 1% ionic groups [Fig. 9(c,d)] revealed a similar trend to that of the TEM micrographs. At lower magnifications of 5 k, the fracture surface of the unmodified [Fig. 9(a)] 70 : 30 PUR/PS IPN appeared rougher than that of the 1% ionic group containing counterpart [Fig. 9(c)]. However, the PS phase domains at 1% incorporation of ionic groups [Fig. 9(d)] were larger than for the corresponding unmodified 70 : 30 PUR/PS IPN [Fig. 9(b)]. From Figure 9(e), the PS phase domain size of the 70 : 30 PUR/PS IPN with 1% ionic groups was found to have ranged from 100 to 400 nm, corroborating the TEM results (100–300 nm). At 2% ionic group incorporation [Fig. 9(f)], the fracture surface was smoother than that of 1% ionic groups [Fig. 9(c)]. The PS domains also decreased in size considerably [Fig. 9(g,h)]. However, even at high magnifications of 50 k [Fig. 9(h)] the formation of a network structure could not be observed due to the limitations of SEM.

CONCLUSIONS

DMTA data revealed a pronounced change in the viscoelastic properties upon the addition of ionic groups. For the 70 : 30 and 60 : 40 PUR/PS IPN compositions, the loss factor data changed from a dominant PUR to a dominant PS peak. The change in the dominant loss factor peak took place at a 2 wt % incorporation of ionic groups. Higher intertransition loss factor values for the IPNs containing ionic groups than for the unmodified counterparts indicated a significant improvement of

IPN phase mixing. The stress-at-break values increased only moderately, whereas a sharp rise in Young's modulus and hardness values was found at 2 wt % ionic groups. The latter was a further indication for some phase continuity of the glassy P(S-MAA) network. At the same time, the strain-at-break values decreased by half. SEM and TEM micrographs indicated a grossly phase-separated morphology for the 70 : 30 PUR/PS IPN without ionic groups. With increasing MAA contents, the PS phase domain sizes decreased considerably. At 2 wt % of ionic groups, TEM micrographs showed interconnected PS phase domains resembling a network structure. At 3% ionic groups a finer network structure was obvious, indicating a further increase in PUR/P(S-MAA) IPN phase mixing.

One of the authors (F.-U.S.) acknowledges a grant from the German Academic Exchange Service, Deutscher Akademischer Austauschdienst, DAAD.

REFERENCES

1. D. Klempner and L. Berkowski, in *Encyclopedia of Polymer Science and Engineering*, Vol. 8, H. Mark, N. M. Bikales, C. G. Overberger, and G. Menges, Eds., Wiley, New York, 1988.
2. L. H. Sperling, in *Interpenetrating Polymer Networks*, ACS 239, D. Klempner, L. H. Sperling, and L. A. Utracki, Eds., American Chemical Society, Washington, DC, 1994.
3. L. H. Sperling, *Interpenetrating Polymer Networks and Related Materials*, Plenum Press, New York, 1981.
4. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, 3rd ed., Wiley, New York, 1989.
5. B. S. Kim, D. S. Lee, and S. C. Kim, *Macromolecules*, **19**, 2589 (1986).
6. D. S. Lee, D. S. Jung, T. H. Kim, and S. C. Kim, *J. Membrane Sci.*, **60**, 233 (1991).
7. D. S. Lee and T. S. Park, *J. Appl. Polym. Sci.*, **43**, 481 (1991).
8. D. S. Lee and T. S. Park, *Polym. J.*, **23**, 241 (1991).
9. D. S. Lee and S. C. Kim, *Macromolecules*, **18**, 2173 (1985).
10. D. S. Lee and S. C. Kim, *Macromolecules*, **17**, 2193 (1984).
11. L. H. Lee and S. C. Kim, *Macromolecules*, **19**, 644 (1986).
12. S. K. Kim and S. C. Kim, *Polym. Bull.*, **23**, 141 (1990).
13. V. Nevissas, J.-M. Widmaier, and G. C. Meyer, *J. Appl. Polym. Sci.*, **36**, 1467 (1988).
14. D. J. Hourston and F.-U. Schäfer, *Polymer*, **37**, 3521 (1996).

15. F.-U. Schäfer, Ph.D. thesis, Loughborough University, Loughborough, UK, 1996.
16. K. H. Hsieh and L. M. Chou, *J. Appl. Polym. Sci.*, **38**, 645 (1989).
17. K. H. Hsieh, L. M. Chou, and S. S. Wong, *Angew. Makromol. Chem.*, **168**, 145 (1989).
18. H. X. Xiao, K. C. Frisch, and H. L. Frisch, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 1035 (1984).
19. E. P. Douglas, A. J. Waddon, and W. J. MacKnight, *Macromolecules*, **27**, 15, 4344 (1994).
20. B. Hird and A. Eisenberg, *Macromolecules*, **25**, 6466 (1992).
21. X.-D. Fan and C. G. Bazuin, *Macromolecules*, **28**, 8209 (1995).
22. A. Eisenberg, P. Smith, and S.-L. Zhou, *Polym. Eng. Sci.*, **22**, 1117 (1982).
23. L. A. Utracki, D. J. Walsh, and R. A. Weiss, in *Multiphase Polymers: Blends and Ionomers*, L. A. Utracki and R. A. Weiss, Eds., ACS Symposium Series 395, American Chemical Society, Washington, DC, 1989.
24. M. Rutkowska, M. Jastrzebska, J.-S. Kim, and A. Eisenberg, *J. Appl. Polym. Sci.*, **48**, 521 (1993).
25. D. J. Hourston and F.-U. Schäfer, *High Perform. Polym.*, **8**, 19 (1996).
26. A. R. Spurr, *J. Ultrastructure Research*, **26**, 31 (1969).
27. K. Kato, *Polym. Eng. Sci.*, **1**, 38 (1967).
28. P. W. Atkins, *Physical Chemistry*, 4th ed., Oxford University Press, Oxford, 1990.
29. A. Eisenberg, *Macromolecules*, **3**, 147 (1970).
30. L. E. Nielsen, *Mechanical Properties of Polymers and Composites*, Vols. 1 and 2, Marcel Dekker, Inc., New York, 1974.
31. D. J. Hourston and F.-U. Schäfer, *J. Appl. Polym. Sci.*, to appear.
32. G. Oertel, *Polyurethane Handbook*, 2nd ed., Carl Hanser Verlag, Munich, 1994.
33. H. X. Xiao, K. C. Frisch, and H. L. Frisch, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 2547 (1984).
34. L. H. Sperling, *Introduction to Physical Polymer Science*, 2nd ed., Wiley, New York, 1992.
35. A. Natansohn, M. Rutkowska, and A. Eisenberg, *Polymer*, **28**, 885 (1987).
36. M. Rutkowska and A. Eisenberg, *J. Appl. Polym. Sci.*, **29**, 755 (1984).
37. D. Acierno, F. P. LaMantia, and G. Polizzotti, *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 1903 (1979).
38. R. W. Dexter, R. Saxon, and D. E. Fiori, *J. Coat. Technol.*, **58**, 43 (1986).
39. J. H. Saunders and K. C. Frisch, *Polyurethanes Chemistry and Technology*, Vol. 1, Interscience Publishers, New York, 1962.
40. S. Rostami, in *Multicomponent Polymer Systems*, I. S. Miles and S. Rostami, Eds., Longman Scientific & Technical, Harlow, UK 1992.
41. X. He, J.-M. Widmaier, and G. C. Meyer, *Polym. Intern.*, **32**, 295 (1993).
42. D. J. Hourston, F.-U. Schäfer, J. S. Bates, and M. H. S. Gradwell, *Polymer*, submitted.