Effect of Acrylic Diblock Copolymer upon Interfacial Adhesion

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SYNOPSIS

The preparation and adhesion properties of poly(methyl methacrylate–butyl acrylate)[P(MMA-*b*-BA)] diblock copolymers have been studied. Block copolymers were analyzed by ^{1}H-NMR, DSC, and SEC, and confirm the synthesis of diblock copolymers, using the iniferter route. Investigation of peel strength in laminate joints, reinforced with various block copolymers, suggests that adhesion depends on both molecular weight and composition. When the copolymer contains mainly PMMA block, molecular weight has a marked effect, with adhesion being enhanced at higher copolymer molecular weight. For other PBA/PMMA compositions, no reinforcement was seen, irrespective of molecular weight. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Interfacial adhesion between polymers is of considerable importance in determining the performance of materials including composites, blends, adhesives, and laminate joints. Various theories have been applied to explain adhesion. According to Wu,[1] the main theories are wetting-adsorption, interdiffusion, chemical reaction, and mechanical interlocking. For adhesion between nonreactive, amorphous polymer pairs, interdiffusion is the main driving force. Direct studies including interfacial profiles,[2] and indirect evidence such as trends of adhesion with time,[3] temperature,[4] and molecular weight,[5] have been studied and are used to support the existence of interdiffusion theories.

At a molecular level, the reptation model[6] can be applied to describe the molecular motion of a single chain. According to de Genes, topological constraints such as entanglement points are created as a result of the inherently long molecules of polymers. These constraints affect chain motions so that chains are confined within "tubes" surrounded by entanglement points. Each chain cannot move across these

points, but tend to move in a curvilinear motion or a snake-like motion, analogous to the migration of defects.

For thermodynamic reasons, adhesion through interdiffusion between polymers is usually poor, due to immiscibility in a binary polymer pair. The interdiffusion is controlled by an energetic factor, characterized by differences in solubility parameter between the two phases. In general, the smaller the difference in solubility parameters, the more miscible the polymers will be. The concept of matching solubility parameters has been very useful in selecting adhesives for plastics.[7] There have been many efforts to strengthen interfacial adhesion in multiphase polymeric systems. In blending technology, one of the most commonly used methods is an incorporation of an interfacial agent or compatibilizer such as diblock, triblock, and graft copolymers, in which one or other segment is identical or miscible with the relevant homopolymers. The ability to lower interfacial tension, promote finer dispersion, and improve the interfacial adhesion are key factors for successful compatibilization.[8]

The role of block copolymers in interfacial adhesion has been studied extensively in a glassy thermoplastic joint. For example, Brown[9] studied the effect of a thin layer of PMMA-*b*-PS diblock copolymer upon adhesion between PMMA and PS and

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found that a doubling in adhesion can be observed. The adhesion varies with the thickness of the block copolymer layer and molecular weight. Kramer[10] studied the mechanism of failure at the polymer interface, in the presence of block copolymers. The degree of polymerization of the block copolymer is an important factor in controlling the failure mechanism. A transition from a chain pull-out mode (low interfacial strength) to chain scission mode (higher interfacial strength) usually occurs over a narrow molecular weight range, or at a critical minimum molecular weight. It was also found that the optimum diblock copolymer molecular weight for a high interfacial toughness is usually between M_e to $4M_e$, where M_e is the molecular weight between entanglements. Interfacial toughness appears to be a product of failure force and the number of diblock copolymers per unit area at the interface. When the product is small, stress is insufficient to cause crazing and so a low toughness results. If the product is greater than the craze stress, crazes initiate and large amounts of energy are lost by growing craze tips. Increases in interfacial toughness with areal density of block copolymer chain at the interface have been observed in PMMA/PPO[11] and PS/PVP[12] polymer pairs.

The present work has centered on the study of interfacial adhesion between a soft acrylic elastomer and rigid poly(methyl methacrylate). Controlling adhesion in this polymer pair is useful in applications such as retroreflective sheeting, pressure-sensitive adhesive tapes or labels, and rubber toughening of PMMA. The patent literature contains several examples of techniques in which adhesion is controlled by, for example, utilizing an adhesive composition containing a reactive group capable of undergoing an *in situ* curing,[13] blending of adhesive with a thermoplastic elastomer to balance tack and adhesive properties,[14] or increasing intermolecular interaction via chemical bonding.[15] However, controlling adhesion via increasing interdiffusion through the use of block copolymer has been seldom reported. The aim of this work is to investigate the effect of P(MMA-b-BA) diblock copolymers upon the interfacial adhesion in the laminate joint.

EXPERIMENTAL

The first step was the preparation of poly(methyl methacrylate–butyl acrylate) block copolymer [P(MMA-b-BA)] with a range of molecular weights and compositions. This was done via a living radical polymerization through the use of iniferter.[16] The

iniferters (*ini*tiator–trans*fer* agent–*ter*minator) refer to initiators that have very high reactivities for chain transfer reaction to the initiator and/or primary radical termination. Most iniferters are organic sulfide compounds with low decomposition energy, such as a benzyl diethyldithiocarbamate (BDC) photoiniferter. Under ultraviolet radiation, the compound splits into a reactive radical and a small radical, which is stable enough not to initiate polymerization but reversibly couples with the propagating chain. After the reaction is quenched, a macroinferter is produced. The macroiniferter can further photodissociate into a reactive propagating radical and a less reactive small radical; therefore, the radical polymerization would proceed via a living mechanism.

Butyl acrylate and methyl acrylate were purified by washing with 5% aqueous sodium hydroxide solution, followed by drying with anhydrous sodium carbonate, and finally reduced pressure distillation. The telechelic polybutyl acrylate, capped with the N,N-diethyldithiocarbamate group was firstly synthesized from a polymerization of butyl acrylate in the presence of an iniferter. Each block copolymer was then synthesized by subsequent polymerization of methyl methacrylate using telechelic PBA as the macroinitiator. The chemical composition, glass transition temperature, molecular weight, and peel strength were then measured.

Iniferter Preparation

The BDC iniferter was synthesized from the reaction between benzyl chloride and sodium diethylcarbamate in absolute ethanol at room temperature.[17] After the reaction was completed, the mixture was extracted from a mixture of dichloromethane and distilled water (1 : 1), three times, and the organic phase was collected, dried with anhydrous sodium carbonate overnight, and solvent removed under reduced pressure.

Block Copolymerization

The copolymerization were carried out in two steps, with the macroiniferter prepared first. The required amount of butyl acrylate was mixed with 0.3 mmol of the BDC iniferter and toluene solvent, the mol ratio of iniferter to monomer were lying between $\frac{1}{150}$ to $\frac{1}{600}$. Oxygen was removed from the mixture by nitrogen purging. The reaction tube was then sealed and exposed to ultraviolet radiation, using a mercury lamp of 254 nm wavelength. The reaction was carried out for up to 12 h in a fume cupboard, after which the product was isolated by double precipi-

tation in methanol, and drying under reduced pressure.

In the second step, the purified polymer was used as a macroiniferter for preparation of the block copolymer. Poly(butyl acrylate) was redissolved into toluene and then the methyl methacrylate was added. The mixture was degassed and the reaction tube sealed before exposure to UV radiation. The reaction conditions were the same as the first step.

Analysis of Block Copolymer

The molecular weight and polydispersity of homopolymer and block copolymers were monitored with SEC apparatus equipped with 10^3, 10^5, and 10^6 Å microstyragel columns, and two detectors, i.e., a Polymer Laboratories (PL) reflactive index detector and PL Low-Angle-Laser-Light-Scattering detector. The SEC apparatus utilized a GBC Instruments LC 1120 HPLC pump operating at room temperature. THF was used as an eluent at 1 mL/min, at room temperature. The DRI detector was calibrated with a polymethyl methacrylate narrow PDi set purchased from PL. Ten standards, 1.14×10^3 to 1.577×10^6 were used to generate a PMMA calibration curve. The data were collected and analyzed using PL Calibre version 6.0 software.

The chemical structure of products was confirmed by ^{1}H-NMR. The spectra were recorded on a Bruker AC300F apparatus, using chloroform-d as a solvent. The composition of the block copolymers were examined by peak integration.

Thermal characteristic of polymers were analyzed by differential scanning calorimetry (DSC). Analyses were performed using TA 2100 software from a Du Pont model 910 DSC module, using a heating rate of 20°C/min, over temperature range of −100 to 180°C.

Evaluation of Adhesion Strength

Solution Casting

Thin films of block copolymer was made by directly casting the copolymer solution onto PMMA sheet, at room temperature, using spin casting. Film of approximately 1 μm average thickness, as estimated from weight of polymer and film dimensions, were prepared. Solutions of 0.37% w/v block copolymer in acetone were prepared. The cast sheet was dried at 60°C for overnight.

Hot Press

HYTEMP 4051 acrylic elastomer was obtained from GEON Australia Limited. A 10 mm wide rubber strip

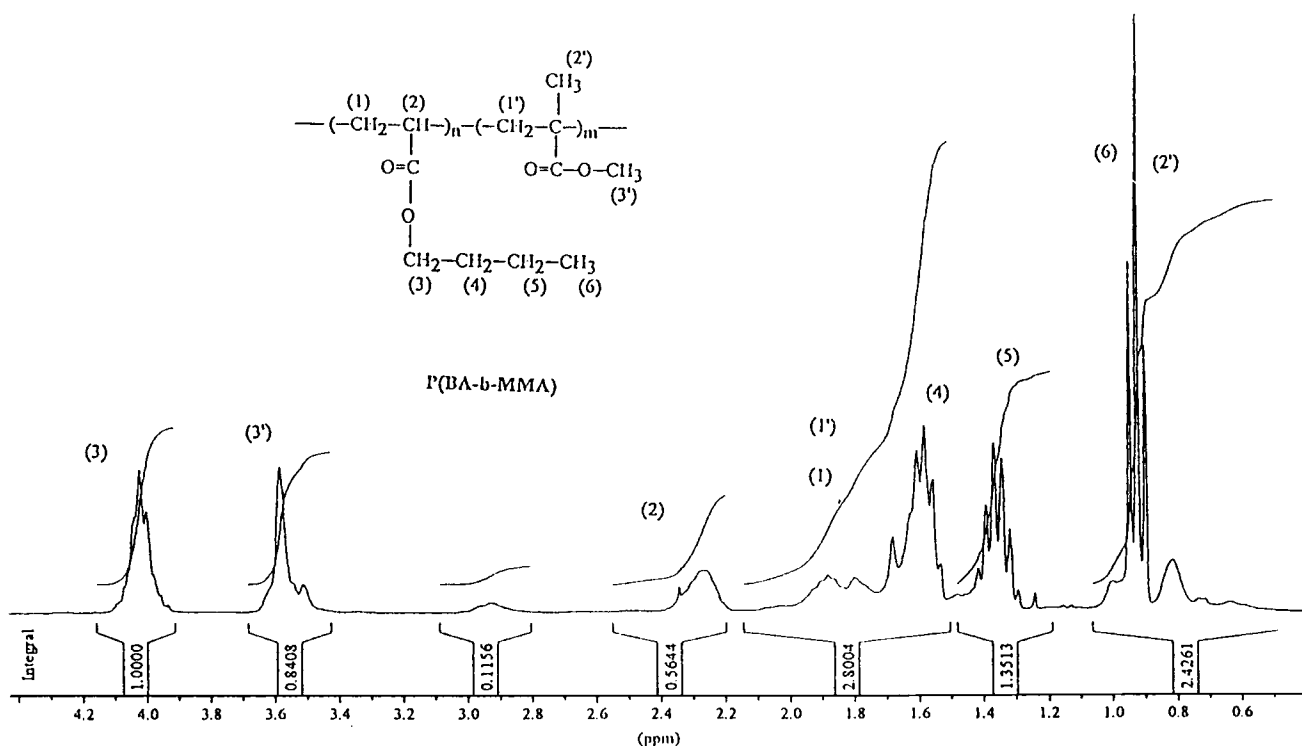**Figure 1** ^{1}H-NMR spectrum of P(MMA-b-BA) block copolymer.

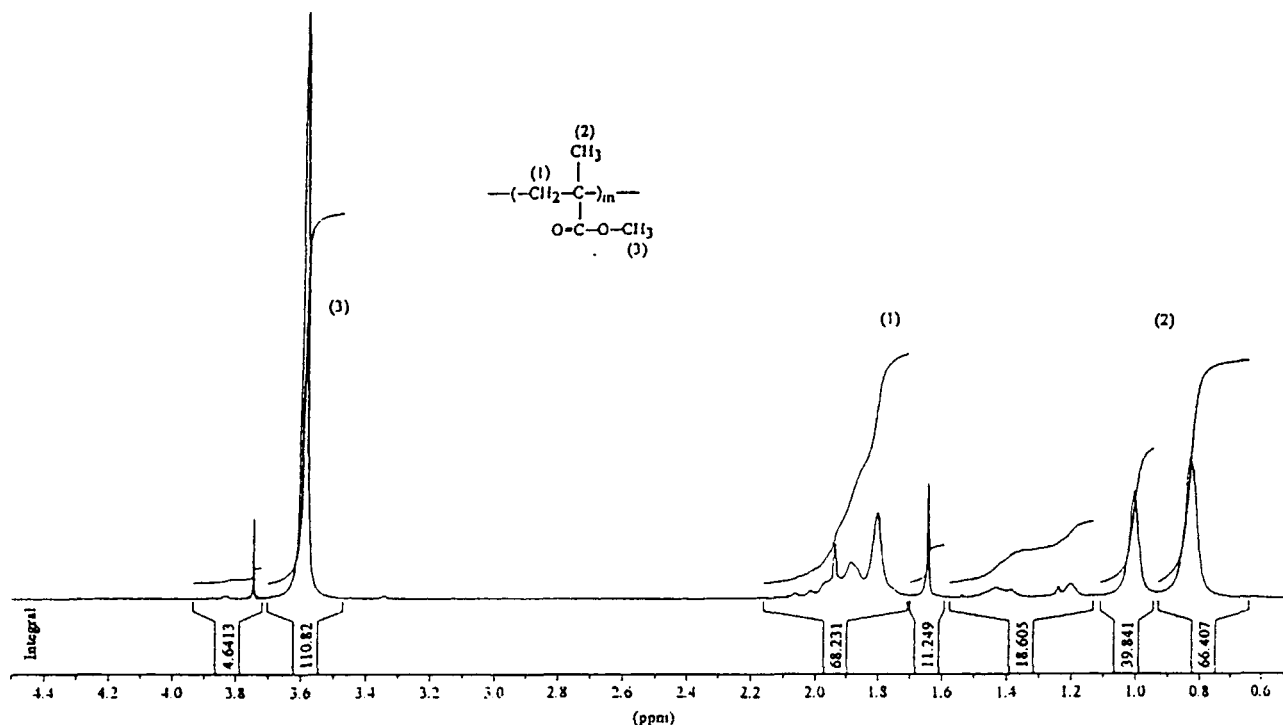**Figure 2** ¹H-NMR spectrum of PMMA.

was prepared and reinforced with backing cloth to avoid energy dissipation through yielding of the rubber strip during peeling tests. The fresh surface of acrylic rubber was brought into contact with the pretreated PMMA sheet in a hydraulic press at 130°C, and 200 kPa for 30 min. The platen was cooled under pressure to room temperature before peel testing.

Peel Test

The adhesion strength of the laminate joint was determined by a 90° peel test, in accordance with the Pressure-Sensitive Adhesive Tape Council PSTC-14 method,[18] with an Instron 1115 universal machine and crosshead speed of 5 cm/min. Adhesion strength P (kN/m) was determined in the usual way, using mean values from five replicated experiments.

RESULTS AND DISCUSSION

Block Copolymerization

Figure 1 shows the ¹H-NMR spectrum of a typical block copolymer with peak identification using correlation data of chemical shifts and NMR spectra catalogs. The two large well-defined resonances at

3.6 (3') ppm and 4.0 ppm (3) are associated with the O—CH₃ (of PMMA) and O—CH₂ (of PBA), respectively. The smallest resonance at 2.9 ppm is characteristic of the O—CH₃ group in the PMMA segment, which is bonded to the other block.[19] The small resonance at 2.95 ppm (2) results from the alpha proton in PMMA. The peaks in the higher field region (0.8–2.0 ppm) appear to be more complicated, due both to coupling and overlapping between protons. For example, the triplet resonance at 0.9 ppm results from CH₃ in the PBA (6) overlapping with CH₃ in the PMMA (2') at 0.8 ppm. The resonance at 1.3 ppm is associated with the CH₂ in PBA (5) coupling with next CH₂ (4) and CH₃ (6) protons. The spectrum for the polymer labeled P(BA-b-MMA) shows characteristic signals of both PMMA and PBA (Figs. 2 and 3), confirming its identity.

¹H-NMR was also used to determine the composition in the block copolymer, by comparing the OCH₂ protons in PBA (3) and the OCH₃ protons in PMMA (3'). The composition of each copolymer was calculated by integration. Percentages of PMMA and PBA were calculated as follows:

$$\% \text{ PBA} = [(n/2)/(n/2 + m/3)] \times 100$$

$$\% \text{ PMMA} = [(m/3)/(n/2) + (m/3)] \times 100$$

Table I Characteristics and Adhesion Properties of P(MMA-*b*-BA) Block Copolymers

Codes	Molecular Weight (M_n)	Polydispersity	PMMA (%)	Average Peel Strength (kN/m)	Standard Deviation
1	73,000	2.9	60	1.40	0.42
2	105,000	3.1	65	1.65	0.37
3	112,000	2.5	90	3.50	0.82
4	115,000	2.0	70	3.30	0.36
5	130,000	1.6	90	3.20	0.43
6	61,000	3.3	20	1.20	0.73
7	68,000	3.8	20	1.27	0.53
8	78,000	1.7	38	1.05	0.19
9	113,000	4.3	30	1.27	0.47
10	245,000	2.2	36	0.82	0.29
11	80,000	3.0	43	1.66	0.46
12	94,000	3.7	48	2.00	0.47
13	97,000	2.8	52	1.56	0.30

where n is the area under the peak at 4.0 ppm and m is the area under the peak at 3.6 ppm.

The characteristics of various block copolymers are summarized in Table I. Block copolymers may be classified into three main groups, i.e., block copolymers with mainly rigid PMMA (>60%), block copolymers with a mainly soft PBA (>60%), and block copolymers of nearly symmetrical structure (40% < PMMA < 60%).

The DSC enables differentiation between block and random copolymers, and a thermogram of a typical block copolymer is shown in Figure 4. These having glass transitions at −43 and 128°C (compared with literature values of −54 and 115°C for PBA and PMMA, respectively[20]). There is good agreement in the T_gs for each segment of the block copolymer and the homopolymers.

The molecular weight of the various copolymers have been analyzed by SEC with LALLS and RI detectors. SEC yields single peaks, with an increase in molecular weight (i.e., lower retention time), upon addition of each second monomer (Fig. 5). Increasing the amount of monomer leads to an increase in MW. An increase in reaction time slightly increases the MW. Control experiments (without iniferter or macroiniferter) were also carried out, under the same conditions, and it was found that no product was obtained, i.e., self-polymerization is negligible. This confirms that MMA does not polymerize readily in the absence of iniferter or macroiniferter.

The results discussed above indicate that synthesis of PMMA–PBA block copolymer, via living radical polymerization through the use of iniferter, is possible. Because the BDC iniferter used is mono-

functional, diblock copolymers are produced. The mechanism of copolymerization is a sequential insertion of monomers between C — S bonds in the compound.[21]

Polydispersities range from 1.5 to 4, much broader than that predicted for a truly living mechanism. For a living radical polymerization, two main types of termination are possible, i.e., reversible and nonreversible termination (i.e., combination of two dithiocarbamyl radical-ended chains). The later case leads to deactivation of the iniferter site or a dead polymer. However, here reversible termination seems to dominate. A study of the living polymerization of butyl acrylate initiated with BDC[22] showed that although a number of side reactions are involved (such as formation of TD by a combination of two dithiocarbamyl radicals, or a nonreversible termination), reversible termination by end-capping of the growing chain by dithiocarbamate group still predominates. This is shown by the high functionality of the polymer, especially at short reaction times.

Adhesion Strength

Figures 6 and 7 show changes in peel strength as block copolymer molecular weight is varied (data points represent an average of 5–10 measurements). The adhesion strength of the control, with no block copolymer, is 1.3 kN/m. Only block copolymers having a high MW and containing a mainly (>60%) PMMA block have a positive effect upon adhesion. In this case, two regimes can be distinguished, at high molecular weight (MW > 110,000) and low molecular weight (MW < 110,000). For the latter,
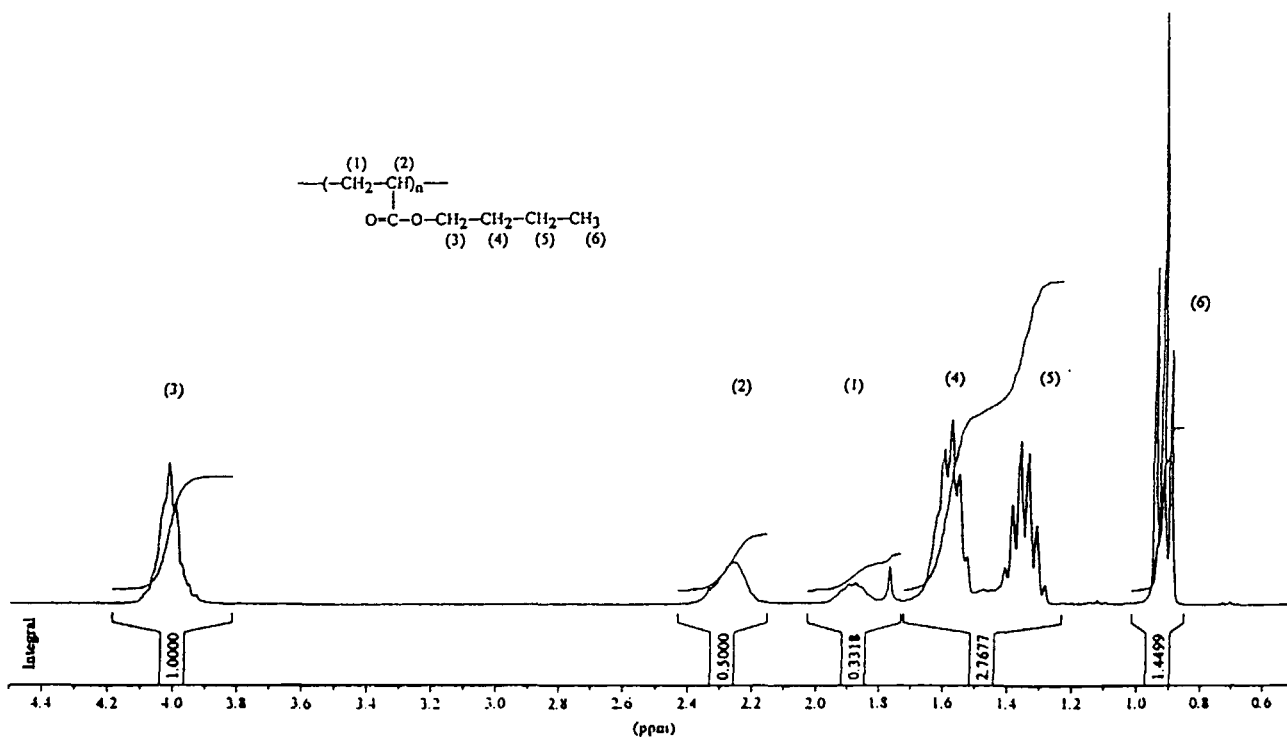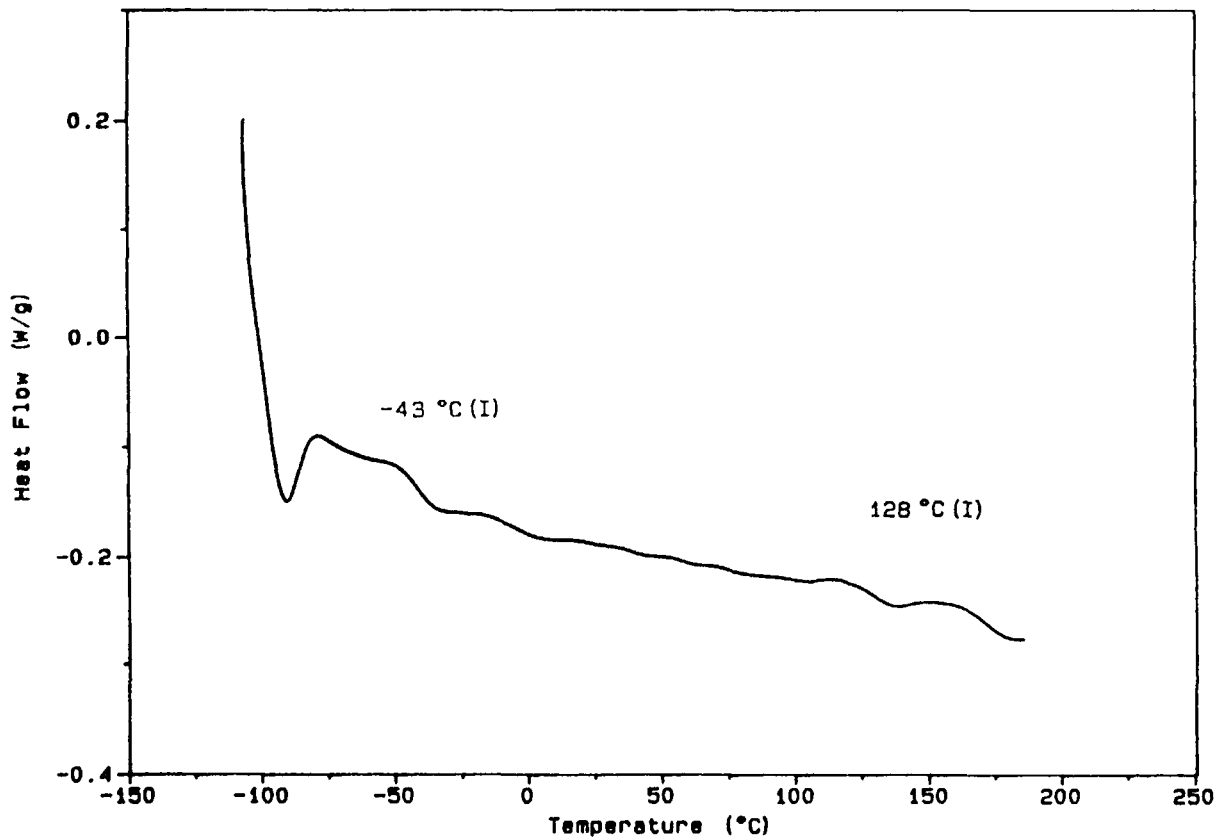
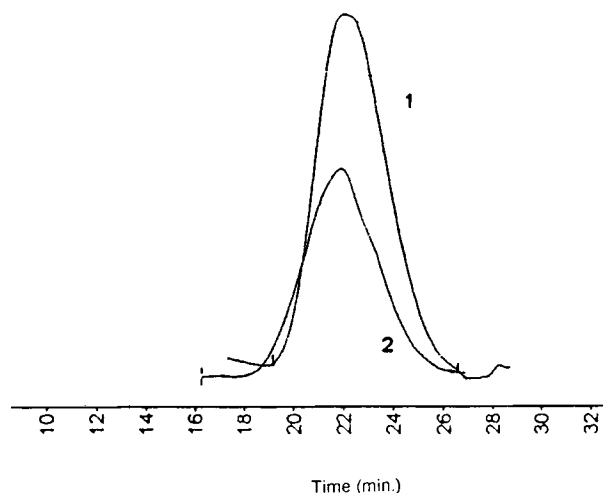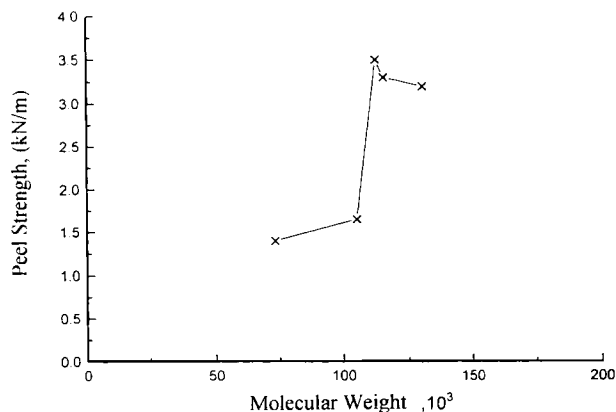**Figure 3**   ¹H-NMR spectrum of PBA.

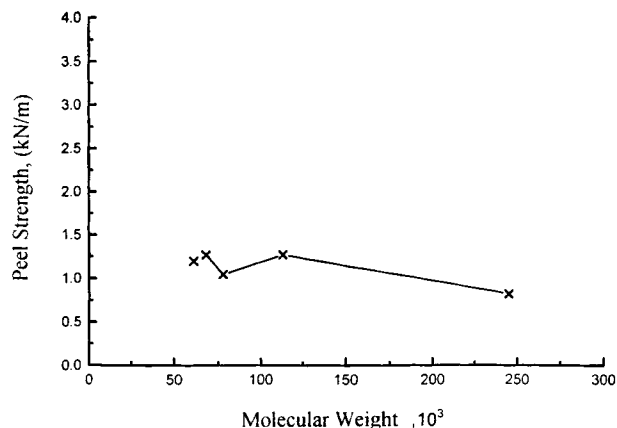**Figure 4**   DSC thermogram of P(MMA-*b*-BA) block copolymer.

Figure 5 Size exclusion chromatograms (SEC) of a poly(butyl acrylate) (1) and the corresponding P(MMA-*b*-BA) diblock copolymer (2); sample 13.

Figure 7 Change of adhesion strength with molecular weight of block copolymers containing mainly PBA.

adhesion is comparable to the control, while for the former, adhesion strength was doubled. Peel force increased steadily with displacement until break (Fig. 8). The transition dependence upon molecular weight appears to be abrupt. In other block copolymers, with less than 60% PMMA, an increase in molecular weight has no significant effect upon adhesion strength, and the peel force trace oscillates (Fig. 9, "stick-slip peeling"), as commonly found for pressure-sensitive adhesives.[23]

Changes in interfacial adhesion are also reflected in surface topography. Scanning electron micrographs of the peeled rubber surface are compared for the two extremes, i.e., the system contain a high MW with mainly PMMA block (Fig. 10) and the system contain a mainly PBA block (Fig. 11). For the first, a rough rupture surface indicates ductile

deformation of the rubber phase near the peel front. In contrast, the SEM of the surface with reinforcing block copolymer contains a smaller percentage of PMMA. The surface is relatively smooth with fewer features, indicating less deformation during separation and weak interfacial adhesion.

The results are consistent with peel test data. The high peel strengths are associated with large energy dissipation through viscoelastic deformation of material around the locus of separation (Fig. 12). With the soft block copolymer, the material is scarcely extendable (Fig. 13) and so peel strength is lower. To examine the locus of failure, PMMA fracture surfaces were also studied by SEM. Typical peeled surfaces of a PMMA/PBA joint reinforced with high MW, a mainly rigid diblock (Fig. 14) and one modified with a mainly soft diblock copolymer (Fig. 15) are shown. The former has second polymer residues, indicating a partially cohesive failure mode. In the

Figure 6 Change in adhesion strength with molecular weight of block copolymers containing mainly PMMA.
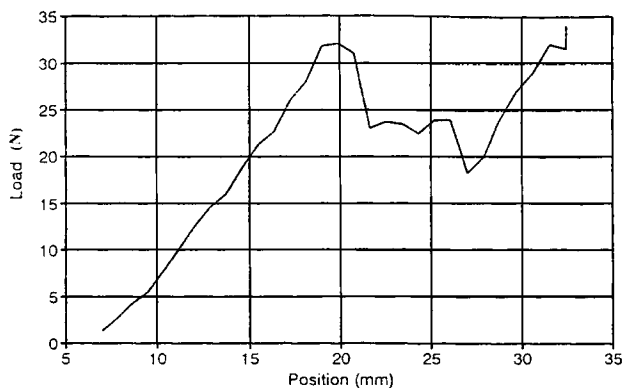
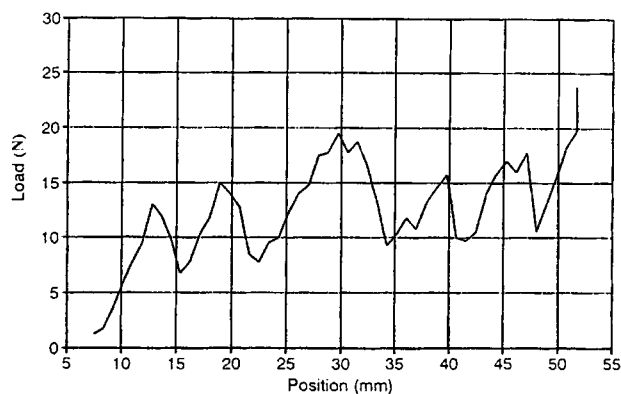**Figure 8** Typical force-displacement peel trace for joint modified with block copolymer 4 (MW = 115,000 and 70% PMMA).

Figure 9 Typical force-displacement peel trace for joint modified with block copolymer 7 (MW = 68,000 and 20% PMMA).

Figure 11 Scanning electron micrograph of peeled surface of rubber, modified with block copolymer 7.
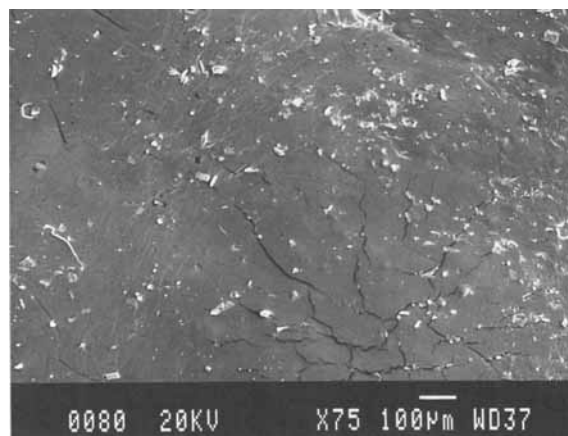
latter case, the surface is relatively clean, indicating interfacial failure.

With block copolymers containing mainly PMMA, molecular weight has a major effect upon the adhesion, consistent with the critical molecular weight concept of Kramer.[10] Here, a minimum degree of polymerization is necessary for good mechanical performance in the immiscible polystyrene (PS)/polyvinyl pyrrolidone (PVP) blend reinforced with PS-b-PVP.

For our acrylic polymers, variation of adhesion strength with MW of block copolymer may be explained as follows. Block copolymers of low MW have insufficient chain length to form effective entanglements between the diblock copolymer chain segment and the homopolymer matrices on each side of the joint, and so interfacial adhesion is weak. On the ot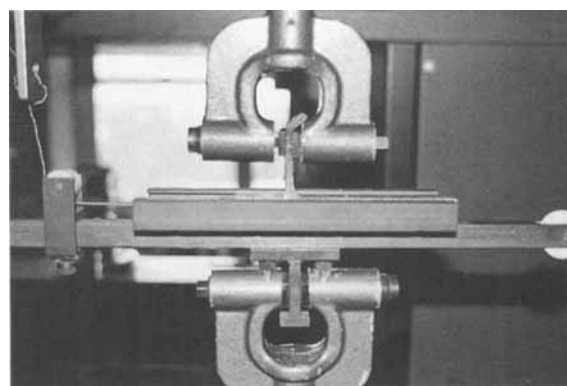her hand, as the MW of the block copolymer become greater, effective entanglement is possible and so interfacial adhesion or peel strength is high.

The failure micromechanism model of polymer interfaces in the presence of block copolymers by Brown[11] are also relevant. Here, it is suggested that interfacial toughness and failure micromechanism are dependent upon the degree of polymerization of block copolymer and its amount at the interface (areal density). Two main mechanisms, chain pull-out and chain scission, can operate, depending on the MW of the block copolymer. Short diblock copolymer molecules will pull out from one side of the interface. On the other hand, if the diblock copolymer molecules are long, failure through chain scission is more likely. This concept has been confirmed by a number of experiments. For example, SIMS experiments with deuterated labels revealed failure mode after deuterium detection in the fracture surface.[24] The amount of block copolymer at the inter-

Figure 10 Scanning electron micrograph of peeled surface of rubber, in a system modified with block copolymer 4.

Figure 12 Peeling behavior of laminate joint modified with block copolymer 4.
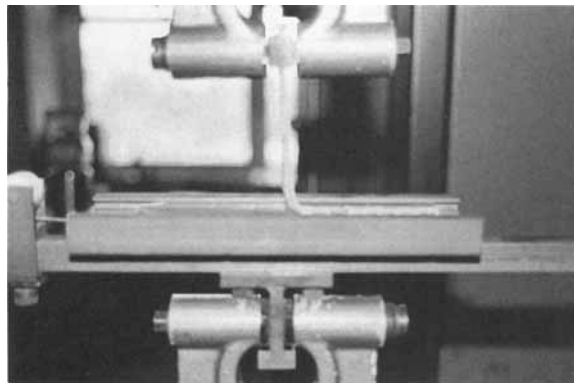
Figure 13 Peeling behavior of laminate joint modified with block copolymer 7.

face is controlled by varying solution concentration during spin casting.

While molecular weight has an important role in adhesion, block copolymer composition is also significant. Block copolymers with less than 60% PMMA do not promote interfacial adhesion, regardless of MW. The polymer interface reinforcement model assumes that block copolymers remain mainly in the interfacial region. In general, the localization of block copolymer at the A/B interface, in the presence of an **a–b** block copolymer, is controlled by enthalpic factors, i.e., the interaction between the block copolymer and the homopolymer matrix. Large values of $_x$aB and $_x$bA, and small $_x$aB, $_x$bA are preferred, in order to encourage the block copolymer to stay at the interface. However, for PMMA and PBA the Flory–Huggins interaction parameter difference is small and so the mixture is partially compatible. Thus, when the block copolymer is incorporated, it appears that the block co-
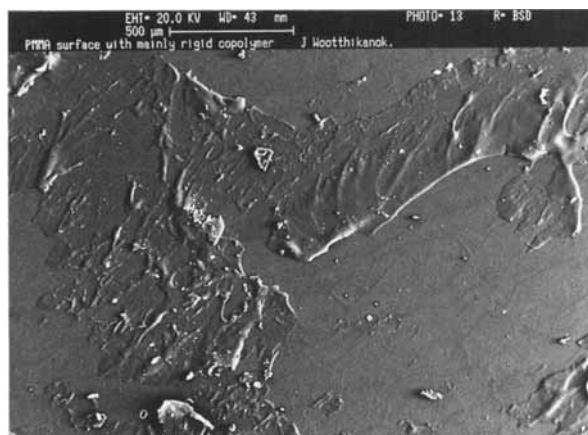
Figure 14 Scanning electron micrograph of peeled surface of PMMA sheet, modified with block copolymer 4.
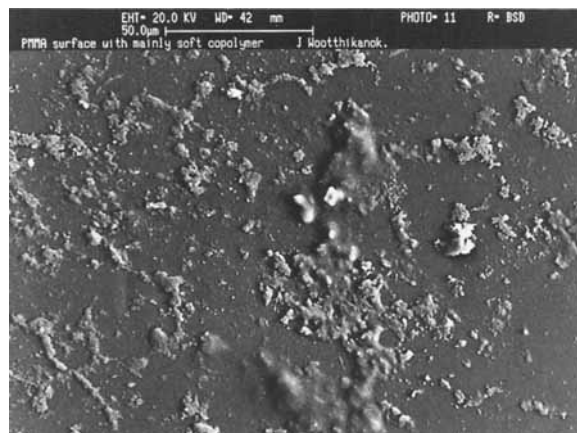
Figure 15 Scanning electron micrograph of peeled surface of PMMA sheet, modified with block copolymer 7.

polymer (after annealing) is poorly fixed in the interfacial region and diffuses into the acrylic elastomer. Preferential migration of the block copolymer into the acrylic elastomer phase is associated with the larger free volume of the acrylic elastomer.

The enthalpic driving force or exothermic/endothermic interaction between phases is a function of many parameters, including the Flory–Huggins interaction parameter, molecular weight, and density. A study of interfacial adhesion in PS/SAN blends reinforced with PS–PMMA copolymer[25] showed that variation of enthalpic interaction with %AN in the SAN can change the minimum MW of a block copolymer required for effective entanglement.

In random copolymers, the PMMA content will affect interaction parameter values for the complete polymer and so a relatively simple prediction for interfacial behavior is possible. In block copolymers, the interaction parameter for the PMMA block remains essentially unchanged, irrespective of PMMA content, and so other factors come into play. These may include changes in phase morphology or chain conformation at the interface. These factors cause the block copolymer to stay at or near the interfacial region, creating effective entanglement between block copolymer and homopolymers.

We are currently pursuing direct methods for imaging the interface, but this is hindered by an absence of chemically selective staining agents to distinguish between PMMA and PBA. However, newer NMR methods[26] appear to have some potential and are currently being explored.

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