

Relationship Between Superficial Response to Environmental Changes and Adhesive Property of Polyurethane Cross-Linked Polyacrylate Network

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SYNOPSIS

A polyacrylic network containing carboxyl groups was cross-linked with polyurethane. The dynamic contact angles (DCA) on specimens were estimated in water. The effect of ingredient ratio and average molecular \bar{M}_n of poly(oxypropylene glycol) (PPG) on DCA were investigated. Data obtained are correlated with 180° peel strength by using the polymer network as an adhesive to adhere both poly(vinyl chloride) (PVC) and polyethylene (PE) film. Results reveal that there is correlation of the surface response to bilateral adhesion of polar and nonpolar substrates. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polymeric materials are characterized by their flexibility. The surface of microphase-separated polymers can respond to changes in the environment via rearrangement of mobile and flexible moieties on the surface. An "intelligent" adhesive based on poly(styrene-hydroxyethyl methacrylate) [P(St-*b*-HEMA)] has been reported that is responsive to substrate polarity. This copolymer adhesive can adhere polar substrates with its PHEMA moiety and nonpolar substrates via its PSt moiety.¹ It is important to elucidate the characteristics of such an "intelligent" adhesive, so a pH-responsive polyurethane cross-linked polyacrylate (PUA) network² was used as a model for studying correlation between dynamic contact angles (DCA) and 180° peel strength of adhered poly(vinyl chloride) (PVC) and polyethylene (PE) with thermoset PUA in this article.

EXPERIMENTAL

Materials

Reagent-grade methyl methacrylate (MMA), ethyl acrylate (EA), hydroxyethyl acrylate (HEA), butylacrylate (BA), and acrylic acid (AA) were used as received. Toluene diisocyanate (TDI) and linear poly(propylene oxide) PPO400 (with $\bar{M}_n = 400$), 1000 (with $\bar{M}_n = 1000$), and 2000 (with $\bar{M}_n = 2000$) were commercially available, whereas benzoyl peroxide (BPO), methyl ethyl ketone (MEK), and acetoxime were of analytical grade.

Synthesis of Polyurethane Cross-linked Polyacrylate (PUA) Network³

Acrylate copolymer (**1**) was prepared from a comonomer mixture of MMA, EA, BA, AA, and HEA at the molar ratio of MMA/EA/BA/AA/HEA = 3.0/2.5/1.17/2.78/0.86 through BPO-initiated polymerization in MEK at 84°C for 5 h. Meanwhile, a polyurethane prepolymer (**2**) was synthesized from TDI and a linear poly(propylene oxide) (PPO) polymer with a —NCO/OH ratio of 2.1 : 1 in MEK. When the —NCO content of the prepolymer

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reached 4.5%, the calculated amount of acetoxime was added and the reaction was maintained at 50°C, preparing the semiblocked polyurethane prepolymer (3).

Poly(acrylate-*g*-urethane) (4) was formed through the reaction of —OH on the HEA unit of polyacrylate (1) with —NCO of the semiblocked prepolymer (3) at the ratio of —OH/—NCO = 2/1 at 50°C for 3 h in MEK. Finally, a cross-linked polymer network (5) was produced by deblocking the cast graft polymer membrane (3) at 110°C for 20–30 min.

Infrared Spectroscopy

A Nicolet 5DX-FTIR spectrophotometer was used to record the spectra of polymer specimens cast from its MEK solution.

Dynamic Contact Angle (DCA) Measurement

The contact angles were measured on the coated slide specimens with the PUA network (5) by dipping a solution of the poly(acrylate-*g*-urethane) (4) in MEK and then deblocking at 120°C for 20 min. Advancing and receding contact angles were obtained based on the Wilhelmy technique using a Cahn Instruments Dynamic Contact Angle Analyzer, DCA-322. The surface tension of distilled water (twice) was determined to be 72.6 dyn/cm. This value was used in the contact angle calculation. The cross-linked specimens were dried by constant weight to estimate DCA. Measurements were carried out for dried specimens and samples after immersing each in water for 20 h.

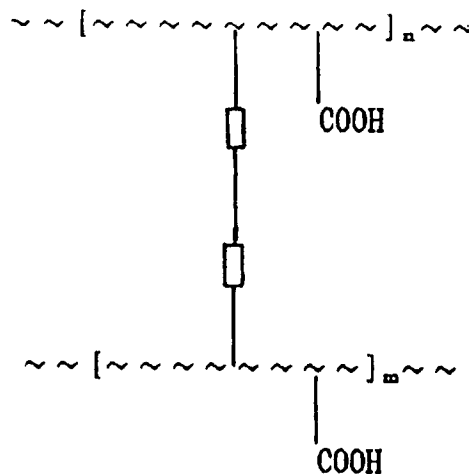
Peel Strength of Films Adhered with the Polymers

PVC–PVC and PE–PE film (25 mm in width) pairs were adhered over 25 mm with the polymers. Peel strength was determined on a fiber tensile tester ZLL-30 at 40 mm/min at 20°C.

RESULTS AND DISCUSSION

Ir Characteristics

The polymer network (5) studied has the following formula:



where polyacrylate moieties $\sim[\sim\sim\sim]\sim$ containing carboxyl group are cross-linked by polyurethane blocked \square .

Figure 1 shows the IR spectra of the polymer network (5) and polyacrylate (1). There are characteristic peaks at 3300 cm^{-1} (N—H stretch vibration), 1938 cm^{-1} (amide II N—H deformation), 1725 cm^{-1} (amide I C=O stretch), and 1599 cm^{-1}

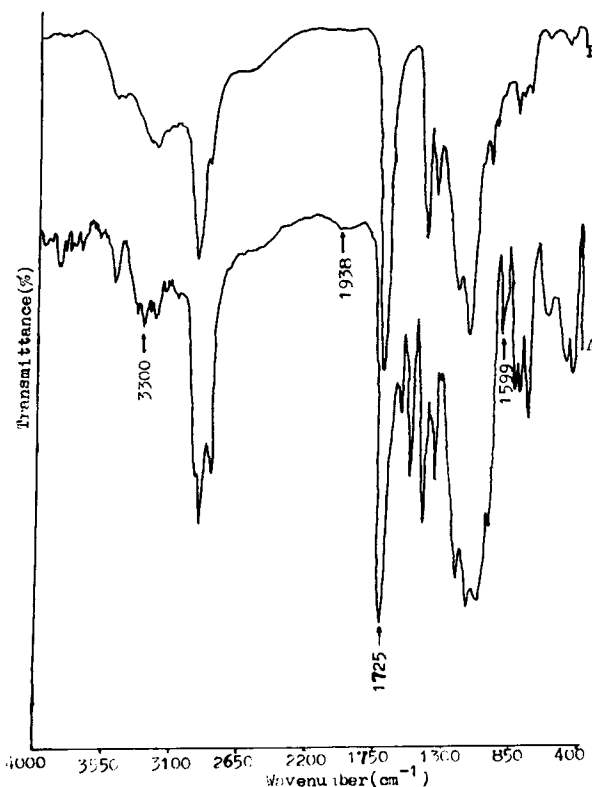


Figure 1 IR spectra of (A) polyurethane cross-linked polyacrylate (PUA) network and (B) polyacrylate.

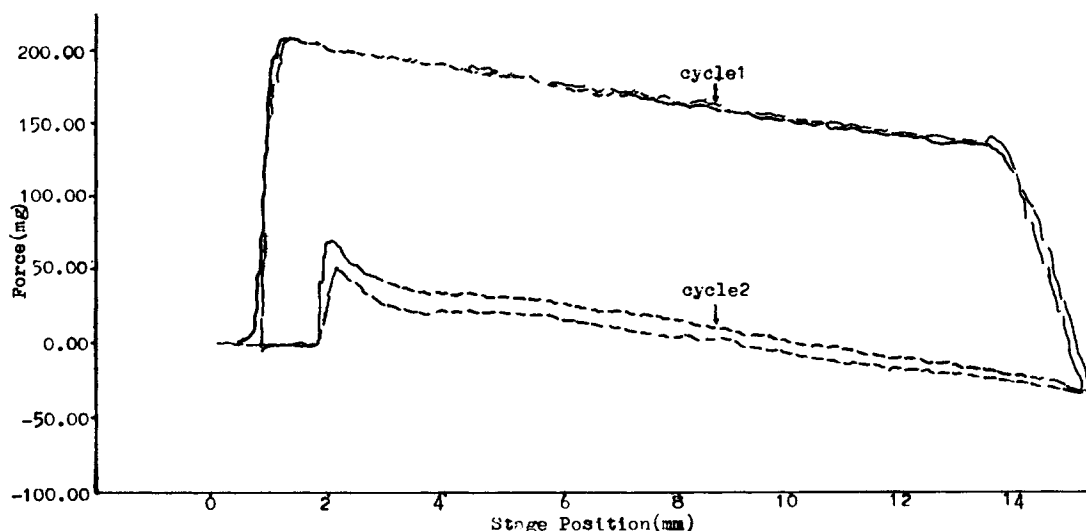


Figure 2 Dynamic contact angle loops for PUA-10.

(phenyl)⁴ in the IR spectrum of (5) in comparison with that of polyacrylate.

Dynamic Contact Angle (DCA)

The Wilhelmy balance technique is a dynamic measurement of the energy of a surface as the slide is immersed into or emerges from water. Initially, the traces of immersion depth vs. force were rapidly

changing as the dry specimen was first placed in water. Figure 2 shows typical dynamic contact angle loops for PUA-10 in which a second immersion, cycle 2, retraces the advancing and receding curves of first cycle. The contact angle hysteresis implies that the specific arrangement of chemical moieties on the surface layer occurs when the surrounding medium changes from air to water and vice versa.

The final results for the PUA polymer network

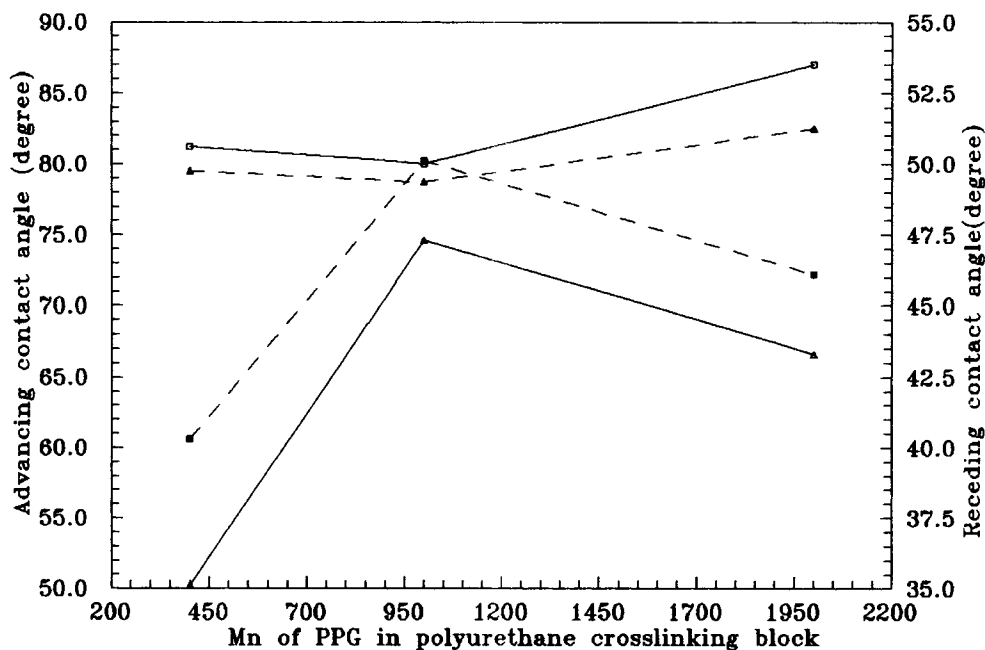


Figure 3 Dynamic contact angle vs. M_n of PPG in polyurethane cross-linking block. Solid line: in air; dashed line: in water. (\square , \blacktriangle) advancing; (\blacksquare , \triangle) receding.

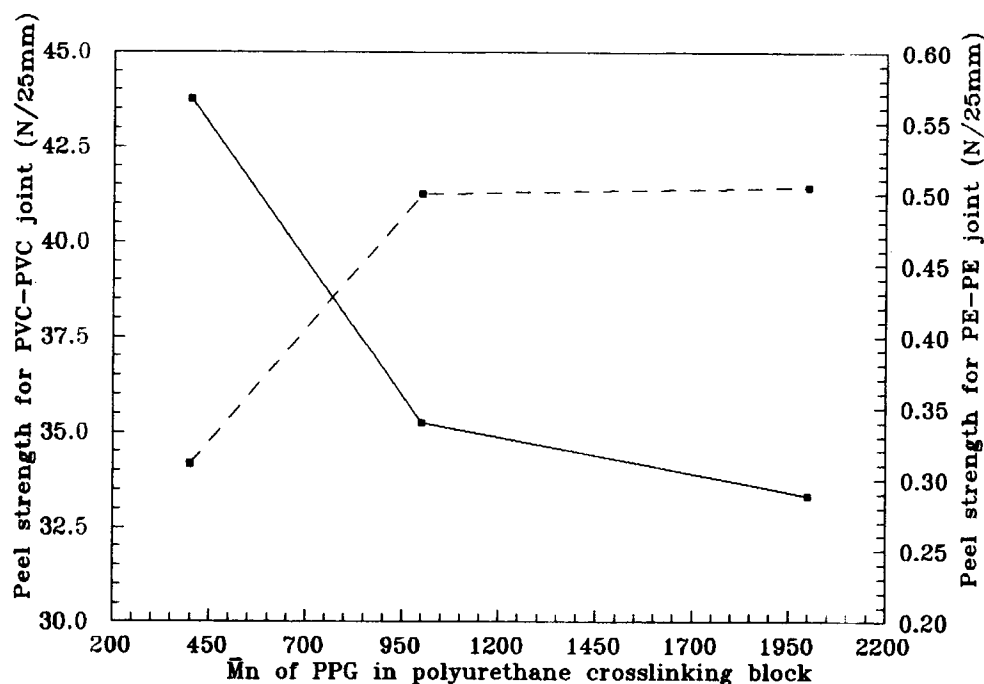


Figure 4 Peel strength vs. \bar{M}_n of PPG in PUA cross-linking block. Solid line is for PVC-PVC joint; dashed line is for PE-PE joint.

are summarized in Figure 3. Comparing dynamic contact angles for dried and immersed specimens reveals that the surface of PUA network exhibits an environmental response that is related to the \bar{M}_n of PPG in the polyurethane crosslinking block. Results reveal that the hydrophilic moieties containing the poly(oxypropylene glycol) (PPG) soft segment concentrate on the network polymer-water interface. The driving force is the strong interaction between water and the hydrophilic groups.⁵ This leads to a decrease in the advancing contact angles, which is largely contributed by the lower surface free-energy component,⁵ e.g., the PUA-10 (with PPG1000) has minimal advancing contact angles of $81.0^\circ \pm 0.2^\circ$ and $78.7^\circ \pm 0.5^\circ$ for the dried and immersed specimens, respectively. At the same time, the receding contact angles increase, which reflects the maximal receding contact angles ($47.3^\circ \pm 0.6^\circ$ and $50^\circ \pm 0.3^\circ$) for the dried and immersed specimens, respectively, because the receding contact angle is sensitive to the higher surface free-energy component, e.g., PUA-10 (with the weight ratio of PA/PU = 3.3 vs. 2.66 for that of PUA-20 composed of PPG2000), which contains a high content of the corresponding hard-segment TDI-cross-linked polyacrylate.

The unique surface characteristics of the PUA-10 polymer network imply that the surface of the network has a better bilateral response to lower and higher surface energy environments, respectively.

Peel Strength of PUA-adhered PE Films

Figure 4 shows the adhesive performance of the PUA network polymer. The data show that the PUA-10 adhesive that has the minimal advancing contact angle exhibits a suitable peel strength for both polar substrate (PVC films) and nonpolar substrate (PE films). This may be attributed to its bilateral responsibility. The polar moiety of the network sensitizes it to polar substrates, whereas the nonpolar moiety of the network accounts for nonpolar ones. Here, an important factor is the adequate response to changes in substrates.

CONCLUSION

Polyurethane cross-linked polyacrylate (PUA) network polymer with a suitable component ratio has

a bilateral surface response to changes in the environment. The network can be designed to be an "intelligent" adhesive for adhering both PVC films and PE films.

The authors acknowledge the support of National Natural Science Foundation of China.

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Received April 5, 1993

Accepted July 27, 1993