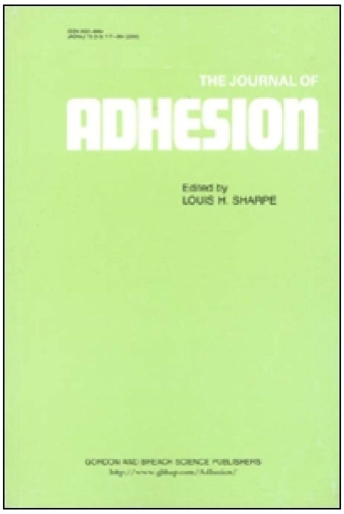

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ADHESION ENHANCEMENT THROUGH CONTROL OF ACID-BASE INTERACTIONS

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ADHESION ENHANCEMENT THROUGH CONTROL OF ACID-BASE INTERACTIONS

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Adhesive bond strengths have been determined for lap-shear joints of PS/LLDPE and PS/CPE, a chlorinated version of polyethylene. Joints were formed at temperatures in the range of 180–280°C. In PS/LLDPE, bond strength at lower joining temperatures is compromised by the inability of LLDPE to act as electron acceptor to the donor properties of PS. However, at $T \geq 260°C$, PS becomes a fluid capable of interacting through dispersion forces only, leading to enhanced diffusion across the PS/LLDPE interface and much stronger adhesive bonds. An acid–base pairing is in effect in joints of PS/CPE, resulting in strong joints made at $T \leq 240°C$. The probable loss of acid-base interaction between the polymers at higher T, coupled with a failure of diffusion across the interface, leads to a lowering of the joint bond strength. Control over interfacial interactions is demonstrated to be a vital factor in the development of adhesive bonds.

Keywords: Adhesion; Acid-base interaction; Temperature-dependence of interaction; Diffusion; Polystyrene; Polyethylene; Modified polyethylene

INTRODUCTION

This article is presented in homage to Wilhelm Neumann, a colleague of many years' standing whose work has provided continuing stimulus

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One of a collection of papers honoring A. W. Neumann, the recipient in February 2004 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M*.

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to workers who, like ourselves, share an interest in the science of polymer surfaces and interfaces. In the current work we continue an inquiry into the role played by interfacial interactions in determining the bond strength of polymer joints. Our view of interactions follows precedents set by Fowkes [1, 2] and Good and coworkers [3], among others, and espouses the protocol of dividing these into dispersive and nondispersive, or acid–base, contributions. The division is not one supported by the bulk of Neumann's work. Instead, he proposes a unified, equation-of-state approach [4] to account for polymer surface and interface phenomena. Neumann's view merits high regard, if for no other reason than because it forces a critical, incisive assessment to be made of the logic of choosing the alternate approach. The ultimate right or wrong of the differing fundamental approaches to polymer surface and interface events will not be settled by the results of this work. In it, notions of acid–base interaction have been adopted simply because they rationalize, perhaps only empirically, the complex characteristics displayed by joints of polystyrene-polyethylene (PS/LLDPE), and of PS/chlorinated polyethylene (CPE), assembled over a significant range of temperatures.

On a number of recent occasions we have used methods of inverse gas chromatography (IGC)[5, 6] to obtain acid (Ka) and base (Kb) interaction numbers for polymers and condensed-phase materials used in polymer compositions. The interaction parameters, which make use of Gutmann's acid–base theory [7], are those originally reported by Saint Flour and Papirer [8] and Schultz *et al*. [9]. In our laboratories they have been applied to phenomena ranging from the dispersion stability of particulates in polymer solutions [10] to the restructuring of surface-localized polymer chains [11]. Most recently [12], we reported an apparent relationship between acid–base interactions at polymer–polymer contacts and the evolution of bond strength, abetted by diffusion across the pertinent interfaces. That work forms the background for the present inquiry, in which the putative relationships to bond strength and to diffusion across the interface are examined by control over acid–base interactions. The systems selected for the purpose are polystyrene/linear, low-density polyethylene (PS/LLDPE) and PS/CPE, the latter a chlorinated version of low density polyethylene. The selection of materials is noteworthy: it places into contact LLDPE, a neutral polymer with a surface where only dispersion, or Lifschitz-van der Waals (L/W) forces are operative and PS, known to be a base. The use of PS is furthered by recent evidence [13], suggesting that its basicity is highly temperature dependent, effectively disappearing at temperatures above about 260°C. Accordingly, control over interactions at PS/LLDPE interfaces should be feasible by choosing appropriate temperatures for contacting the polymers. A second method for controlling interactions was the use of CPE films, the surfaces of which had been modified by exposure to corona discharge treatment. The effects of controlled interactions were monitored by bond strength determinations on single lap-shear joints.

EXPERIMENTAL

Materials

The LLDPE was an octene copolymer, obtained from AT Plastics Inc. It had a reported melt flow index of 2.2 and was compounded with 0.15 wt% Santanox® antioxidant. The PS, obtained from Dow Chemical Co. (Midland, MI, USA) had an $Mw = 4.6 \times 10^4$ and an $Mn = 3.9 \times 10^4$ (from size exclusion chromatography). CPE was donated by Dow Chemicals Canada (Samia, Ontario, Canada). XPS analysis showed this to have a Cl/C ratio of 0.11.

Procedures

The polymers were compression molded at 190°C in a Carver press to form sheets 1.0 mm in thickness. Sheets of CPE were surface modified by exposure to a corona discharge, utilizing equipment described in an earlier communication [14]. The applied potential was 12 KV, and exposure time was limited to 20 seconds. Following formation, sheets of the polymers were placed in desiccators under a dry nitrogen atmosphere for 48 h prior to further use. Polymer samples to be bonded, 22 × 12 cm in size, were cut from the molded sheets and formed into single lap-shear joints in which the bonded area was 72 cm^2. Lap-shear specimen were formed in the Carver press at temperatures ranging from 180–280°C. The applied load, maintained for 5 min, was about 150 kg/cm^2. Bonded specimens were quenched under cold running water, dried and stored for 24 h under ambient conditions before being evaluated with an Instron table model tester (Instron, Canton, MA, USA) at a jaw separation speed of 5.0 mm/min. Some of the bonded joints were aged in a vacuum oven under controlled conditions of time and temperature prior to testing. In all cases at least 2, and generally 3, separate determinations of bond strength were carried out. The experimental uncertainty in these measurements did not exceed ±5%.

Surface characterization of the polymers made use of IGC in the case of PS and CPE. Additional surface analysis of all polymers was based on contact angle measurements. IGC measurements were carried out with a Varian, 3400 chromatograph (Variau, Palo Alto, CA, USA), equipped with both hot wire and ionizing flame detectors. As in the preceding study [12], the PS was deposited from solution onto Chromosorb® AW 60/80 support (Chromatographic Specialties, Cornwall, Ontario, Canada). Deposition from (xylene) solution was practiced with CPE. Conventional drying and ashing procedures showed that deposited polymer accounted for 8.8 wt% of the total stationary phase in the case of PS and 9.3 wt% for CPE. Solids were housed in previously washed and dried stainless steel columns. The stationary phases were equilibrated under flowing He (at 15 mL/min) for 24 h prior to experimentation. Probe molecules included the n-alkanes from pentane through octane, and benzene, dichloromethane, ethyl acetate, and tetrahydrofuran. The latter probes were selected from Gutmann's listing of vapors for which acceptor and donor numbers were available [7]. Frequently described procedures [8, 9, 12] were followed to determine retention volumes and subsequently, the acid (Ka) and base (Kb) characterization parameters. These were measured over the 180–280°C temperature interval. The experimental uncertainty attached to the Ka and Kb parameters rises from ±4% at temperatures below 240°C to ±8% at the highest temperatures relevant to this work. Contact angle determinations utilized a Ramé-Hart goniometer, (Ramé Hart, Mt. Lakes, NJ, USA) equilibrated at 24°C. Distilled water was the contact fluid. As described previously [15], data were accumulated over a period of 20 min. and extrapolated to zero contact time. The determinations carry an uncertainty not exceeding 2°.

RESULTS AND DISCUSSION

The procedures of this work called for polymer samples to be exposed to elevated temperatures for significant times. This applied both to joint formation exercises and, more particularly, to the aging of assemblies to be used in studies of (postulated) polymer chain diffusion across interfaces.

A requisite to this work, therefore, was assurance that no serious chemical modification arose in the course of elevated temperature operations. The contact angle data in Table 1 relate to the question. The contact angles for water on PS and on LLDPE do show a very slight downward shift as the severity of time/temperature exposure increases, but the maximum change (4° for both polymers) lies just at the border of the experimental reproducibility of determination. It seems reasonable to conclude that any thermally induced chemical

TABLE 1 Effect of Temperature-Exposure Time on Contact Angles: Water on PS and LLDPE

Exposure T (°C)	Exposure time (min)	Contact angle (o) PS	LLDPE
60	10	77	92
180	10	76	91
180	150	76	89
200	10	75	90
220	20	75	91
220	60	73	90
220	150	73	88
260	10	74	89
280	10	73	88

All contact angle measurements at 24°C.

changes in the polymer surfaces were very slight and unlikely to have affected the bond characteristics of the assemblies.

The bond strengths of PS/LLDPE and of PS/CPE assemblies made over the temperature range designated above are shown in Figure 1. They respond to temperature variation in dramatically different ways. Where the bond strength of PS/LLDPE joints increases with rising bond formation T by a total of about 62%, that of PS/CPE decreases by some 27%, from 6.3 MPa for joints made at 180°C to about 4.6 MPa for those made at 280°C. Noteworthy is the progression of bond strength in both cases. The gradual, nearly linear rise in bond strength for PS/LLDPE in the interval 180–240°C changes to a more pronounced upward trend for joints made at 260 and 280°C. In the case of PS/CPE, bond strength at first remains largely insensitive to bond formation T, but displays a distinct downward trend in precisely the T range in which PS/LLDPE bond strength increases nonlinearly.

The PS/LLDPE System

Of the two trends in Figure 1, that for PS/LLDPE is more evidently consistent with the interaction phenomena under present discussion. As already stated, the PS is a net base, with a Kb value near room temperature of about 1.8 and a Ka near 0.2 [12]. At lower temperatures, then, a PS/LLDPE interface involves a mismatch *in kind* of interaction forces, limiting the degree to which intimate contact between chain elements can be established and limiting also the strength of adhesive bonds. The interaction parameters, however,

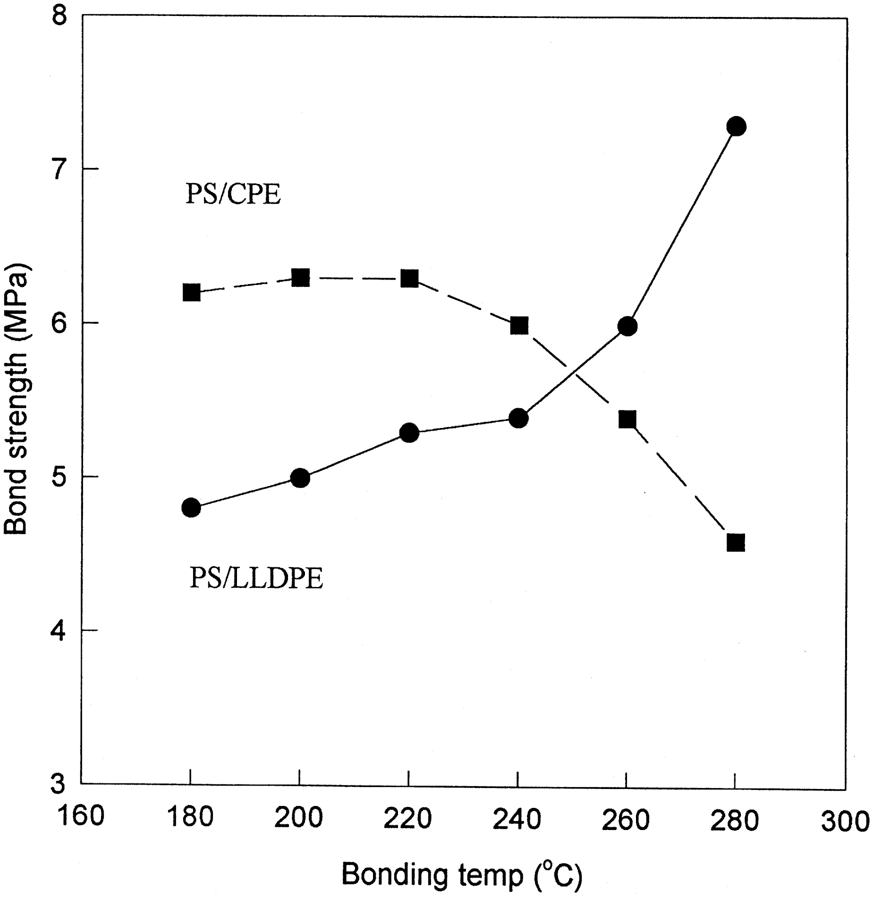

FIGURE 1 Variation, with bonding temperature, of bond strengths in PS/LLDPE and PS/CPE.

are temperature sensitive, as shown in Figure 2, where the total interaction potential of PS, (Ka + Kb), is plotted against temperature. The abatement is effectively linear and, given the experimental error inherent in the IGC data from which the parameters are obtained, reduces the acid-base interaction potential of the polymer to zero in the 240–260°C interval. As a result, in accord with our expressed postulate, when PS and LLDPE are brought into contact at T ≥ 250°C, °C, only L/W forces should be operative across the interface. The L/W forces, albeit reduced by some 10% at these elevated temperatures as compared with their strength at ambient temperatures, remain attractive, arguing in favor of more intimate mixing by way of

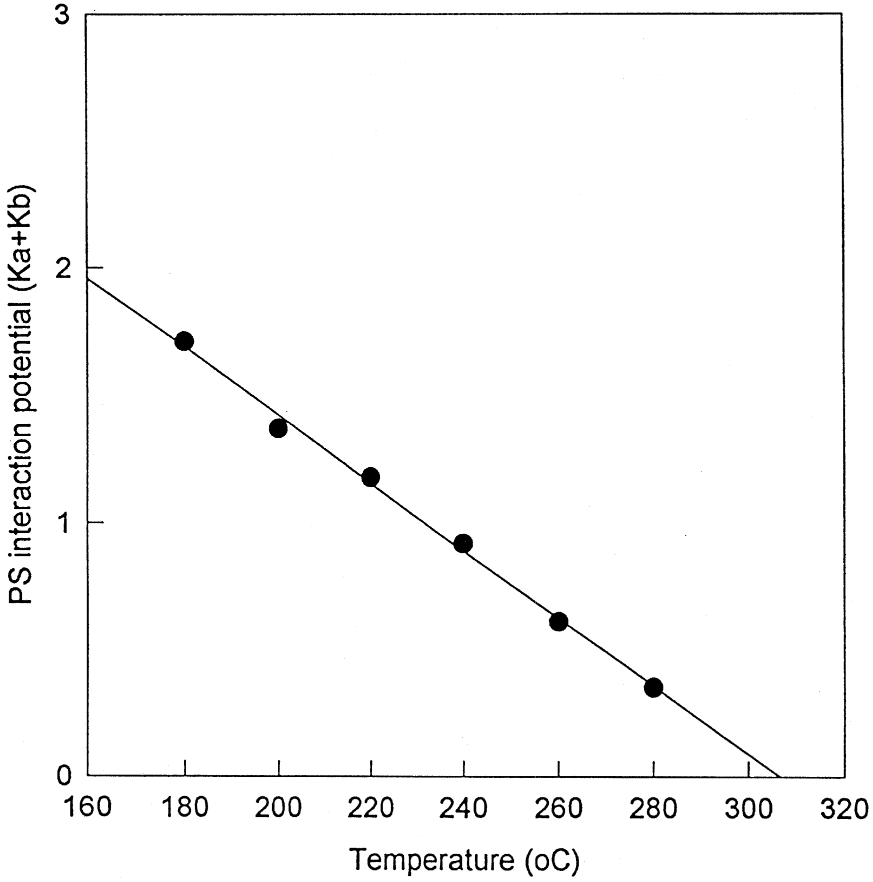

FIGURE 2 Temperature dependence of total acid–base interaction potential of PS.

diffusion across the interface and the consequence of an enhanced adhesive bond. The stated cause–effect argument logically calls for the existence of a functional dependence between bond strength and the total interaction potential of PS. The expectation is met, as shown in Figure 3. The semilogarithmic representation was chosen purely for reasons of convenience and, at this stage, cannot be accorded any theoretical significance. Were it possible to reduce the interaction potential to the extrapolated zero, then a strong (cohesively failing) bond near 10 MPa might be expected. In terms of present experiments this would entail bonding temperatures above 300°C and the inherent risk of unacceptable thermo-chemical artifacts.

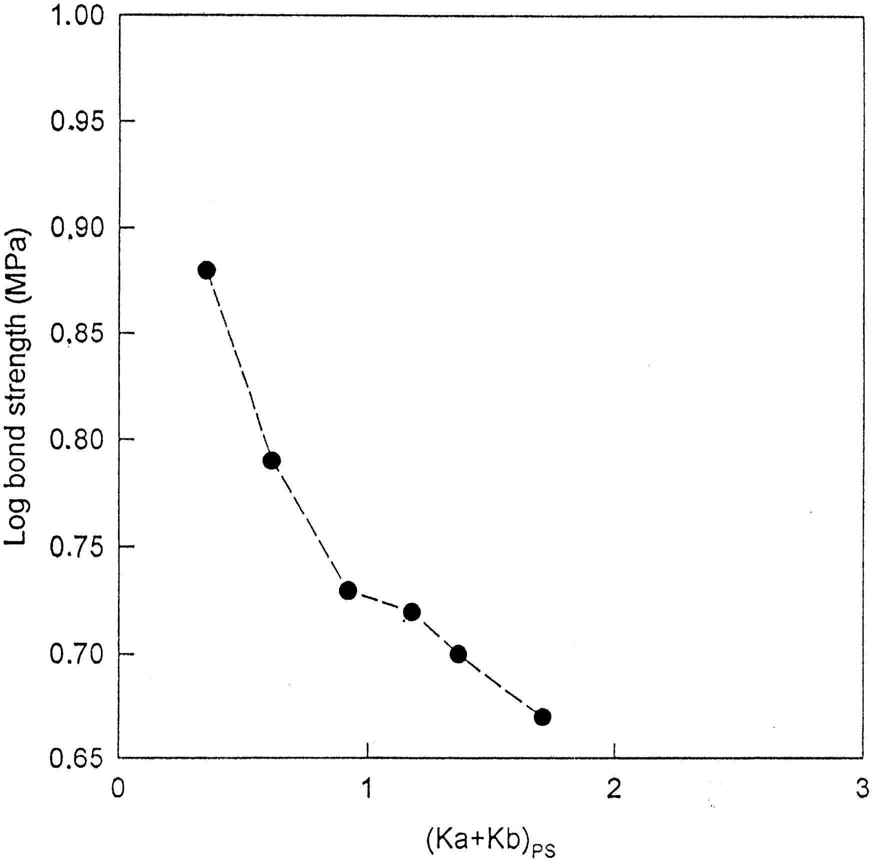

FIGURE 3 Sensitivity of bond strength in PS/LLDPE to total acid–base interaction potential of PS.

Viewed from the results in Figures 1 and 3, the bond characteristics of PS/LLDPE appear to implicate a mechanism of diffusion across the polymer interface to form an interphase [16]. The formation of an interphase, of course, calls for the degree of contact intimacy postulated to occur at and above the “critical” 250°C boundary. In other words, while some degree of interfacial diffusion may take place below a bonding temperature of 250°C, the maximum bond strength attained in this work, 7.6 MPa for joints bonded at 280°C, should be unattainable in joints made at lower temperatures, even when allowed to age at temperatures well above the (about 100°C) Tg of the PS constituent. The data of Figure 4 are to the point of the matter. Here are

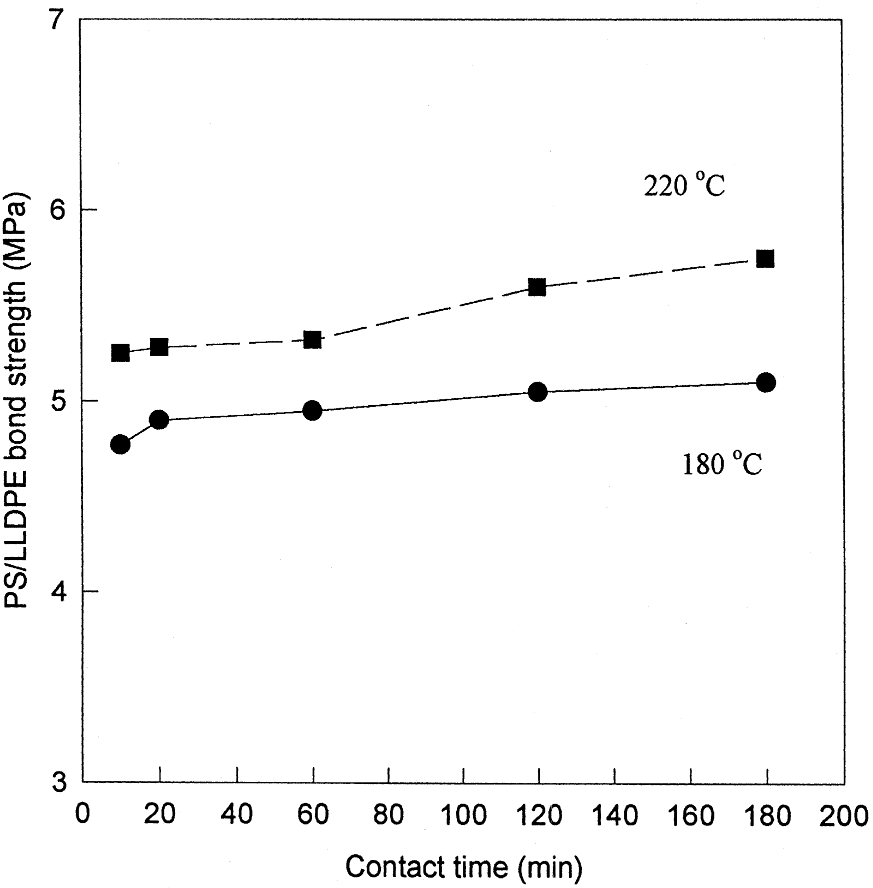

FIGURE 4 Effect of aging at 160°C on bond strength of PS/LLDPE joined at 180°C and 220°C.

shown the bond strengths of joints bonded at 180°C and at 220°C, which had been aged at 160°C for up to 3 h, a time seemingly sufficient to allow for interdiffusion, but at a temperature where the short-range interaction forces of PS remain significant. The respective increments in bond strengths of 6 and 11% are considered to be above the bounds of experimental error but fall far short of the massive increase shown in Figure 1. Apparently, under conditions favoring the persistence of short-range acid–base forces in PS, the success of chain transfer across the PS/LLDPE interface is limited.

The PS/CPE System

In order to further consider the performance of this system, it is useful to compare the surface properties of LLDPE and CPE. The results given in Table 2 serve the purpose. The tabled surface energies show the CPE to have a somewhat higher total surface energy (γ_t) than the LLDPE. The difference is almost totally due to the presence, in CPE, of a significant contribution from γ_{ab}, the acid-base component of surface energy. That this is largely attributable to acidic surface linkages is implied by the IGC results, which assign a finite Ka value to the polymer, Kb being essentially negligible. Surface acidity arises from the surface presence of Cl in the polymer, and the current result is in excellent agreement with analytic data reported in a previous communication [17]. Of course, the data for CPE are not characteristic of the present, corona-treated version of the polymer. However, corona treatments are recognized as imparting surface acidity to olefinic polymers [18, 19], wherefore the assumption of retained surface acidity in the present specimens is reasonable. As in the case of PS, the interaction potential of CPE is T dependent, as shown in Figure 5. The downward progression in Ka with rising temperature is nearly linear and becomes negligible near 290°C. In the assemblies made at temperatures where a–b forces remain finite there is contact between an acidic and a basic polymer, a situation that should favor the formation of strong adhesive joints. Returning to Figure 1, clearly the bond strengths of PS/CPE joints surpass those of their PS/LLDPE counterparts at bonding temperatures up to about 240°C. (Note, however, that they fail to attain the high bond strengths of PS/LLDPE bonded at the highest temperatures of this work). The decrease in bond strength at higher bonding temperatures is open to some conjecture: Since both PS and CPE have reduced specific interaction potentials at these temperatures, contact should be between essentially neutral polymers where interfacial mixing might be expected to produce a strong bond, a

TABLE 2 Comparison of Surface Properties of LLDPE and CPE

	LLDPE	CPE*
γ_d (mJ/m^2)	30.6	30.9
γ_{ab} (mJ/m^2)	0.3	2.4
γ_t (mJ/m^2)	30.9	33.3
Ka	—	3.1
Kb	—	0.6

*Applies to “as received” polymer, prior to corona treatment.

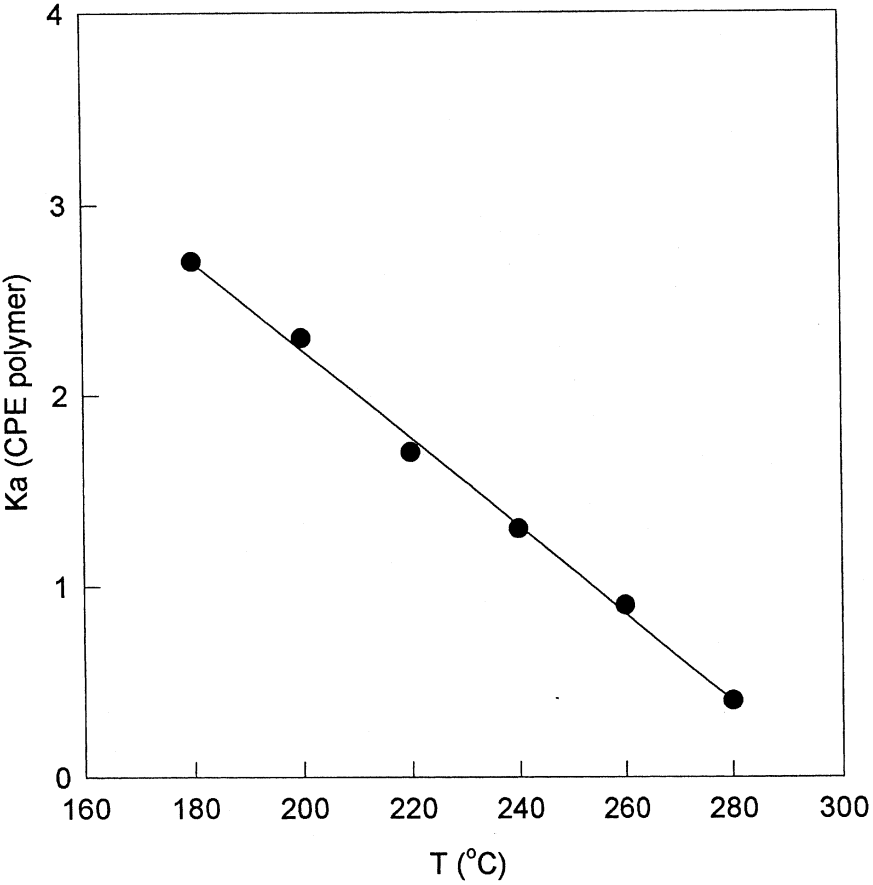

FIGURE 5 Temperature dependence of Ka in CPE (in "as received" state).

suggestion inconsistent with the trend in Figure 1. Of course, it may be argued that simple L/W interaction would not produce the high bond strengths attainable when favorable a–b interaction can take place. Another consideration must be taken in account, however. The tabled surface characteristics of CPE, as already noted, pertain to the material in its "as received" state, whereas the bonded assemblies used the CPE following corona treatment. The temperature dependence of interaction parameters for corona-modified CPE is not measurable by the methods of this report. If corona-treated CPE were to retain its acidity over the pertinent temperature range, there may then be the less favorable contact between a "neutral" PS and the still acidic CPE, the reverse of the situation postulated for the PS/LLDPE. However, the surface characteristics in Table 2 tell only a part of the story. It is well known that corona discharge treatments of polyolefins, in addition to favoring surface acidification, result in surface-localized crosslinking [18, 19]. The CPE surface may have a very high surface viscosity throughout the experimental T range, and this would inhibit any transfer of chain elements across the interface. Thus, the lower-than-expected values of bond strength in Figure 1 at T up to 240°C may be attributable to the failure of diffusion across the interface in creating a reinforcing interphase. Then, at higher temperatures, if the T dependence of Ka for CPE is unaffected by corona treatment, the matter is made worse by the loss of surface-localized a–b exchanges between the polymers.

An inquiry into postulated diffusion contributions to bond strength followed the precedent set for the PS/LLDPE combination by exposing joints made at 180 and at 240°C to aging at 160°C for up to 3 h. The results of the aging procedure are given in Figure 6. There is more scatter in the bond strength data for this system, but there is no discernible rise in the bond strength over the exposure period. Even if present, diffusion mechanisms appear to play a negligible role in establishing the bond characteristics of this system.

CONCLUSION

Control over interfacial interactions in joints of polystyrene (PS) and linear low-density polyethylene (LLDPE) was exercised by selecting bonding temperatures in which the PS can act as a net base (below about 250°C) or a fluid capable of interacting through dispersion forces alone (above the given temperature). It was shown that substantial enhancement of the adhesive bond can be realized by joining the polymers at temperatures where the PS acts as a nonpolar substance, thereby avoiding contact between the neutral polyolefin and an electron donor.

Diffusion across the interface, leading to the formation of an interphase, is cited as a contributor to the stronger bond under these conditions. In a second approach to controlled interfacial interaction the PS was joined to CPE, an acidic component. Here, acid–base interaction promoted the formation of strong adhesive joints when bonding took place at appropriate, lower temperatures. At higher temperatures bond strengths decreased for reasons which, to a degree, remain speculative. In part they reflect the loss of acid-base interaction, the PS and (speculatively) the CPE becoming capable of exerting

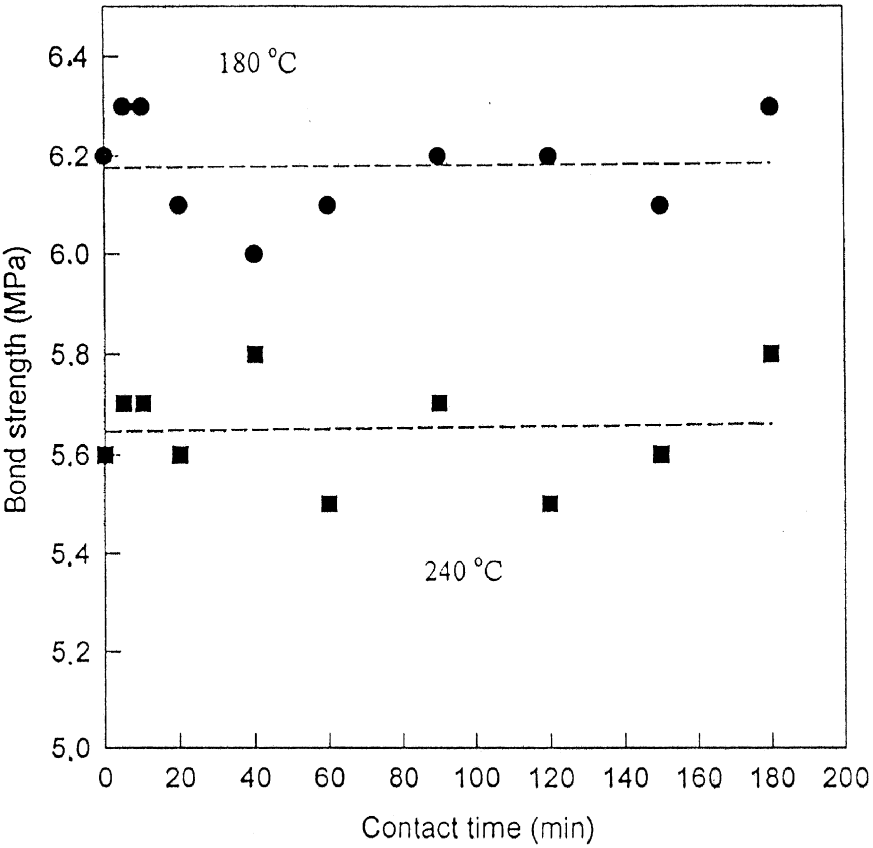

FIGURE 6 Effect of aging at 160°C on bond strength of PS/CPE joined at 180°C and 240°C.

only dispersion force interactions. In part, they may also reflect the failure of diffusion to occur across the interface of a system in which one component (CPE) retains a high surface viscosity. Regardless of a full rationalization for these results, control over acid–base interaction in the course of polymer joining has been demonstrated to exert major influence over the strength of bonds achieved.

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