Durability of Green Polyurethane Adhesive Bonded Aluminum Alloy in Dry and Hydrothermal Ageing Conditions

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ABSTRACT: Polyurethane (PU) adhesives were prepared from the reaction of polycaprolactone (PCL) polyols based on palm kernel oil based polyesteramide (PPKO) with an aromatic and cycloaliphatic diisocyanate. Four different formulations of PU adhesives were prepared by varying the NCO : OH ratio, in order to investigate the effects of NCO : OH ratios on adhesion strength. The adhesive strength of metal–metal bonding both in dry and hydrothermal ageing—was determined by single lap shear joint testing. The resistance to hydrolysis of the PU adhesives was determined by performing water absorption tests. The water absorption test samples suggested that the durability of the adhesives correlated to lower water absorption due to higher NCO content. The correlation between the crosslinking of the PU network and adhesive strength was also studied by performing swelling tests. The higher NCO content showed that, the higher crosslink density of PUs led to higher cohesion and adhesion strengths. PU1.7 showed optimal properties in terms of durability and resistance to hydrolysis, whereas PU2.0 revealed deterioration in durability and resistance to hydrolysis due to the presence of greater micro-voids content in the PU2.0 matrix. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41151.

INTRODUCTION

In recent years, polymer adhesives have increasingly been used in many structural engineering applications. Polyurethane (PU) adhesive is a polymeric condensation produced in a chemical reaction between polyol and diisocyanate, and is considered to be one of the most important structural adhesives. One of the major factors limiting the application of adhesive bonding technology is the degradation in joint strength often observed when exposure to hot, humid environments occurs. Studies on the durability of adhesives have been given more and more attention, especially when adhesives are being used in aggressive environments, such as those with high moisture content, extreme temperatures, aggressive chemicals, mechanical stresses, and a combination of these factors. Early work by Sharpe[1] also indicates that exposure under stress substantially increases the degradation process.

Moisture is the substance that causes the greatest difficulties for many adhesives, sealants, and coatings, in terms of environmental stability. Moisture often causes swelling and degradation (hydrolytic),[2] and that degradation is closely related to water absorption.[3] It is believed that the water absorbed by adhesively bonded joints can deteriorate the strength and performance of the joints by damaging the adhesive–substrate interfacial region and the adhesive itself.[4–6] Hydrolytic degradation is greatly influenced by a number of factors including the chemical properties of polymer material, ageing temperature, and ageing time.[7–9] High temperature accelerates the diffusion of moisture and the ageing process. Boubakri[10] investigated the effect of moisture absorption and hydrothermal or hygrothermal ageing on the mechanical properties of thermoplastic PU (TPU). They reported that the amount of diffusion of water molecules into the sample largely depends upon the ageing temperature, and this factor in turn affects the mechanical properties of TPU. Aglan[11] also found that the modulus of elastomeric PU decreases with ageing time.

Before the mechanisms of hydrolysis can occur, the moisture (or water) must find its way into the bulk polymer or the interface between the adhesive and the substrate.[12] The presence of voids in the polymer matrix allow for water penetration. A higher rate of water absorption might suggest the greater presence of void content in the polymer.[13]

This article deals with the investigation of the effect of NCO : OH ratio (1.3, 1.5, 1.7, and 2.0) on the PU adhesion strength for both unaged (dry) and hydrothermally aged samples. In addition, this paper focused on the correlation between crosslink densities as well as water absorption, and durability, plus the resistance to hydrolysis of PU adhesives based on polycaprolactone (PCL) polyol.

EXPERIMENTAL

Materials

A PCL polyol based on PPKO with a hydroxyl value of 522 and a molecular weight of 754 Daltons was prepared earlier using a method described in the previous study.[14] 2,4-diphenyl methylene diisocyanate (MDI) with an NCO content of 31% was obtained from Maskimi Polyols Sdn. Bhd., bis(4-isocyanotocyclohexyl) methane (H$_{12}$MDI) with an NCO content of 32%, propylene carbonate (PC), and ethanol were purchased from Sigma Aldrich. ɤ-Glycidoxypropyltrimethoxysilane A 187 (ɤ-GPS) was supplied by Momentive.

Preparation of the Aluminum Substrate

An aluminum alloy was used as a substrate, i.e., AA2024-T3. The substrates were cut according to ASTM D1002-72 with dimensions of 25.4 mm × 102 mm × 1.6 mm. The surface of the substrates was ground using a 600 grit abrasive paper. The surface of the substrates was wiped clean with a tissue and soaked with acetone in order to remove grease, dirt, and other foreign matter. Then, the substrates were treated in warm water (50°C) for 30 min, rinsed with distilled water, and dried in ambient air. Aluminum was then dipped in 1% ɤ-GPS solution for the duration of 5 min to achieve a surface silanization. This solution was prepared with a ratio of 1 mL ɤ-GPS to 99 mL ethanol, and then it was stirred continuously for 30 min. The silane films were then dried in ambient air and held at a temperature of 110°C for 30 min. This silane film acts as an adhesion promoter in adhesive bonding.

Preparation of Polyurethane Adhesive

The PU adhesives were prepared in a clean, dry paper cup. Two types of isocyanate (MDI and H$_{12}$MDI with a ratio of 65 : 35) were added to the requisite amount of polyol resin. The ratio of NCO to OH was also varied from 1.3, 1.5, 1.7, to 2.0; thus, the samples of PU adhesives were labeled PU1.3, PU1.5, PU1.7, and PU2.0, respectively. The mixture was mixed well using a mechanical stirrer at 1000 rpm for about 15 s and then applied immediately to the substrates using a brush. Then, the adhesive bonding was cured in an oven at a temperature of 120°C for 1 h.

Characteristics of the Polyurethane Adhesive

Working life of the adhesive is the period a resin or adhesive will remain usable after the two-components, i.e., polyol resin and isocyanate were mixed together. About 5 g of each PU adhesives (PU1.3, PU1.5, PU1.7, and PU2.0) were placed in a test tube and stirred with a glass rod until the adhesive mixture gelled and stick to the glass rod. The time from beginning until the adhesive gelled and stick to the glass rod was recorded as the pot life or working life of PU adhesive.

Swelling tests are often used to measure the crosslink density of elastomers. When a cross-linked polymer is immersed in an appropriate solvent, the polymer imbibes the solvent and swells. The amount of solvent imbibed and the degree of swelling is dependent upon the crosslink density of polymer networks; the greater the crosslink density, the less swelling.[15] Adhesive film specimens were placed in toluene for 48 h. The swollen specimens were then removed from the solvent. The solvent was gently wiped off before the specimens were weighed. From the weight of the swollen polymer (w_s), volume fraction of swollen polymer (V_p) can be calculated by eq. (1):[15]

$$V_p = (w_d/d_p)/[(w_s/d_s) + (w_d/d_p)] \qquad (1)$$

where w_d is the dry weight, d_p and d_s are the densities of solvent and the polymer, respectively. Crosslink density (n) values were obtained from V_p with the Flory-Rehner equation as in eq. (2)[16,17]:

$$-\left[\ln\left(1 - V_p\right) + V_p + \chi V_p^2 \right] = V_s n \left[V_p^{1/3} - \left(V_p/2\right) \right] \qquad (2)$$

where V_s is the molar volume of the solvent and χ is the polymer–solvent interaction parameter which could be found from eq. (3)[16,17]:

$$\chi = (\delta_1 - \delta_2)^2 V_s / RT \qquad (3)$$

where R is the gas constant and T is the absolute temperature, whereas δ_1 and δ_2 are solubility parameters of solvent (toluene = 18.2 MPa$^{1/2}$) and polymer (PU = 20.5 MPa$^{1/2}$).[16]

Hydrolysis tests were carried out, in order to evaluate the stability and resistance of the PU adhesives to hydrolytic attack. Resistance to hydrolysis was estimated using two different methods—water absorption test and a shear test measuring the durability of adhesive joints. Water absorption was carried out according to ASTM570-98. PU samples were weighed before some samples were placed in 25°C and some in 70°C water for 7 days. The percentage of water absorbed by the PU samples was calculated using the following equation:

$$W\% = [(W_w - W_d)/W_d] \times 100 \qquad (4)$$

where W_d is the weight of dry polymer and W_w is the weight of the polymer after water absorption. Changes in the weight of wet samples should not exceed 5%.[18]

The shear test measuring the durability of adhesive joints was carried out according to ASTM D2919-01. The preparation of the specimens was similar to ASTM D1002-72, which is used for single lap shear tests. The overlapped area was 12.7 × 25.4 mm^2. The substrates were aligned and pressed with clips. A 1 kg load was placed on the joint to squeeze out any extra resin until a uniform thickness of 0.1 mm was achieved. Then, the PU adhesive/aluminum bonding samples were cured in an oven at a temperature of 120°C for 1 h.

Half of the bonded specimens were then immersed in distilled water at a temperature of 25°C and another half were immersed in distilled water at a temperature of 70°C for 7 days. The testing of the hydrothermal aged specimens was carried out using the Universal Testing Machine model, Instron, equipped with a 30 kN load cell capable of measuring the lap shear strength of the Al joints. The crosshead speed was kept at 5 mm/min. The
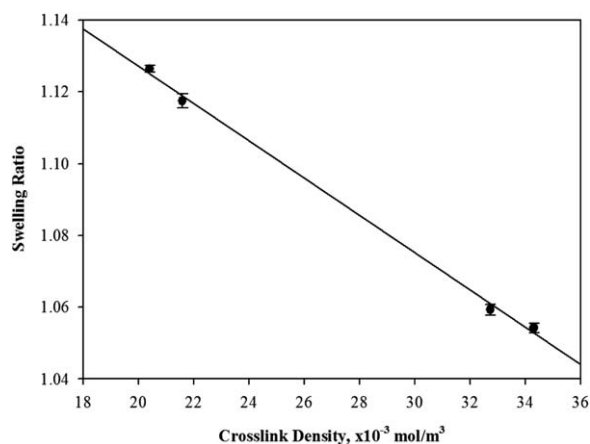
Figure 1. The dependence of the swelling ratio on the crosslink density of PU adhesives.
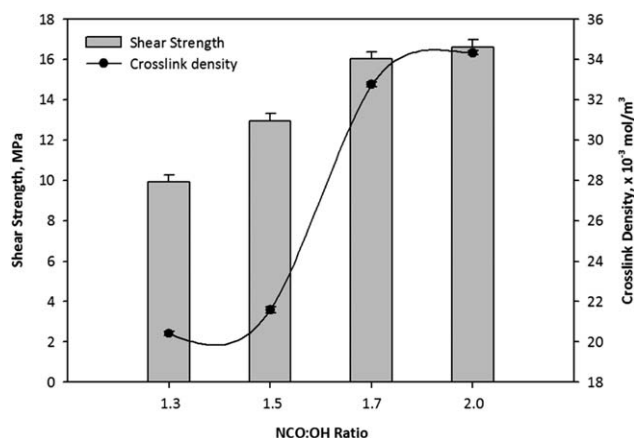

Figure 3. FTIR spectra of PU adhesive. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shear stress was evaluated by the formula: $\tau = P/A$, where P is the tensile load, and A is the overlapped area of the joint. The fractured surfaces were characterized for microstructural by using Zeiss Supra 40VP field emission scanning electron microscopy (FESEM).

Attenuated total reflection Fourier transform infrared (FTIR-ATR) spectroscopy (Perkin Elmer model 400) was used to measure the FTIR spectra of the PU samples at a wavelength of 4000–650 cm^{-1}. From two stretching regions of the spectrum, i.e., carbonyl (C=O) and amide (N—H), the ratio of hydrogen bonding can be quantified by eqs. (5) and (6), respectively:[19]
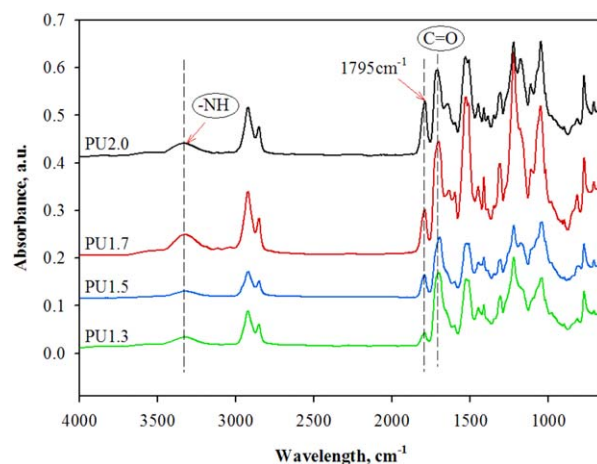
$$R_1 = A_{H-CO}/(A_{H-CO} + A_{f-CO}) = A_{1703}/(A_{1703} + A_{1738}) \quad (5)$$

$$R_2 = A_{H-NH}/(A_{H-NH} + A_{f-NH}) = A_{3325}/(A_{3325} + A_{3445}) \quad (6)$$

where R_1 is the ratio of hydrogen bonded carbonyl group and R_2 is the ratio of the hydrogen bonded N—H group. A is the area under the peak with a corresponding wavelength.

RESULTS AND DISCUSSION

Correlation and Interaction Between Structures—Properties of Polyurethane Adhesive

The results of the swelling test demonstrate that the crosslink density value of PU adhesives significantly decreases with an increase of swelling ratio, q, which is the ratio of the volume of swollen to unswollen polymer and can be defined as the reciprocal value of the volume fraction of swollen polymer, V_P.[20] Figure 1 shows the dependence of the swelling ratio on the crosslink density of PU adhesives. The results support the basic theoretical principle of the crosslink density of elastomer—the greater the crosslink density, the less ability the polymer network has to imbibe solvent.

The effect of the NCO : OH ratio on crosslink density and its correlation to the lap shear strength of PU adhesives are shown in Figure 2. Figure 2 illustrates how the crosslink density gradually increases as the ratio of NCO increases. This indicates that the NCO : OH ratio affects the rigidity and the crosslink density of the PU network. Higher NCO content yields a densely crosslinked structure and corresponds to better adhesive bond strength. This bonding strength also correlates to hydrogen bonding in PU network.

The extent of hydrogen bonding in PUs can be studied quantitatively by determining the ratio of hydrogen bonding (R) via FTIR. Figure 3 shows the comparative FTIR spectra for PU adhesives at various NCO : OH ratios. Table I gives a detailed list of absorption frequencies (wavelengths) for various groups, as well as their hydrogen bonded complexes. PUs are extensively hydrogen bonded, with the proton donor being from the N—H group of the urethane linkage. The hydrogen-bond acceptor may be in either the hard segment (the carbonyl of the urethane group) or the soft segment (an ester carbonyl or ester oxygen).[21]

The deconvoluted peak values for A and calculated values of R_1 and R_2 are presented in Table II. As presented in Table II, R_1, and R_2 show a similar trend with PU1.7 as with the optimum. FTIR results prove that the theory of the relationship between the degree of hydrogen bonding and adhesive bonding strength

Figure 2. The effect of the NCO : OH ratio on the crosslink density and shear strength of PU adhesives.

Table I. The Characteristics of IR Absorption Frequencies for Polyurethanes[21,31]

Wavelength (cm^{-1})	Bonding	Group
3445–3450	Free	N—H
3315–3340	Hydrogen bonded	N—H
3260–3290	Oxygen (ether) bonded	N—H
1730–1740	Free	C=O (urethane)
1703–1720	Hydrogen bonded	C=O (urethane, carbonate)
1775–1820	Free	C=O (Aryl Carbonate)

is true. The higher the degree or ratio of hydrogen bonding, the higher the bonding strength of PU adhesive.

A new peak appeared at wavelength 1795 cm^{-1} (Figure 3), referring to the stretching of free carbonyl of the aryl carbonate (urethane). Aryl carbonate (urethane) is formed in the reaction between propylene carbonate and amine, which gives a carbamate structure containing a secondary hydroxyl (OH) group. This secondary OH group then reacts with an isocyanate to form aryl carbonate (urethane). As the NCO : OH ratio increases, the intensity of aryl carbonate (urethane) increases. This result indicates that the number of carbonyl groups in the PU network is greater as the ratio increases. This is one possible explanation as to the highest shear strength of unaged PU2.0.

Water Absorption Influences the Adhesive Bonding Strength
The percentage of water absorption ($W\%$) of PU adhesives at various NCO : OH ratios are shown in Table III. At 25°C, the $W\%$ decreases as the NCO : OH ratio increases. The results are more interesting where there is no water absorbed for PU1.7; however, when the NCO : OH ratio increases to 2.0, the $W\%$ is about 0.07%. A similar trend is observed for samples that were immersed in 70°C water; the $W\%$ decreases until the NCO : OH ratio is 1.7 and increases as the ratio is increased to 2.0. These results may be related to the formation of micro-voids in the polymer matrix during the curing process, which allowed for water penetration. The higher value of $W\%$ might suggest the presence of a greater void content in the polymer,[13] causing an imperfect interfacial bonding between the two phases. The FESEM images of fractured surfaces (Figures 4 and 5) show that the content of micro-voids in PU2.0 is greater than PU1.7.

The micro-voids may correlate to the working life of the PU adhesives. It was observed that PU2.0 has the shortest working life (Table I). The micro-voids, which resemble bubbles of foam, may not have had enough time to be removed from the polymer matrix during the curing process. Furthermore, stresses generated by the difference in the thermal expansion coefficient between the PU adhesives and the Al substrate may have enhanced the moisture absorption at the interphase. Besides the normal diffusion mechanism, it is suspected that the capillary transport of water molecules into the interface between adhesive and substrate potentially occurred.[23]

The absorbed water molecules filled the spaces between molecules of the polymer. This phenomenon creates a force to separate macromolecules resulting in PU adhesive to expand. Furthermore, the increase in chain separation causes the forces of secondary bonding between the molecules decreases. Some researchers reported that the water absorption in the adhesive bonding can reduce the strength and influence the fatigue properties of the joints by destroying the adhesive-substrate interface,[4–6] especially when the adhesive bonds were exposed in the hydrothermal medium.

Figure 6 shows the effect of the hydrothermal ageing on PU adhesive bonding at various NCO : OH ratios after exposure to water of 25°C and 70°C for 1 week. In comparison to unaged PUs, the bonding strengths of hydrothermal aged PUs are slightly decreased where the percentages of strength reduction were about $0.96 \pm 0.7\%$ (PU 1.3), $1.01 \pm 0.5\%$ (PU 1.5), $0.18 \pm 0.1\%$ (PU 1.7) and $4.71 \pm 0.5\%$ (PU 2.0) at a temperature of 25°C. Percentage of reduction in shear strength is found increasing in the ageing temperature of 70°C where shear strength for PU 1.3, PU1.5, PU1.7, and PU 2.0 decreased by $9.18 \pm 0.7\%$, $7.76 \pm 0.5\%$, $4.08 \pm 1.0\%$, and $11.1 \pm 0.4\%$, respectively. This indicates that when the NCO : OH ratio increases, the resistance to hydrolysis of PU adhesives also increases. PU1.7 demonstrates the optimal stability to hydrolysis, whereas PU2.0 shows a decrease in the strength retention. This means that PU2.0's stability in hydrolysis and the hydrothermal ageing is worse than other PU adhesives with lower NCO : OH ratios. This problem is exacerbated by temperature.

Fracture Surfaces Analysis
FESEM images with low magnification (100×) of fractured surfaces are displayed in Figures 7–9. Figure 7 shows micrographs of a fractured surface of unaged PU samples; meanwhile Figure 8 presents micrographs of a fractured surface of hydrothermal aged PU samples in water at temperature of 25°C. Figure 9 indicates micrographs of a fractured surface of hydrothermal aged PU samples in water at temperature of 70°C. Figure 7 presents a combination of adhesive and cohesive failures (mixed-mode failure) obtained for all PU samples except PU1.7.

Table II. The Hydrogen Bonding Ratio of Carbonyl and N—H Group for PU Adhesives

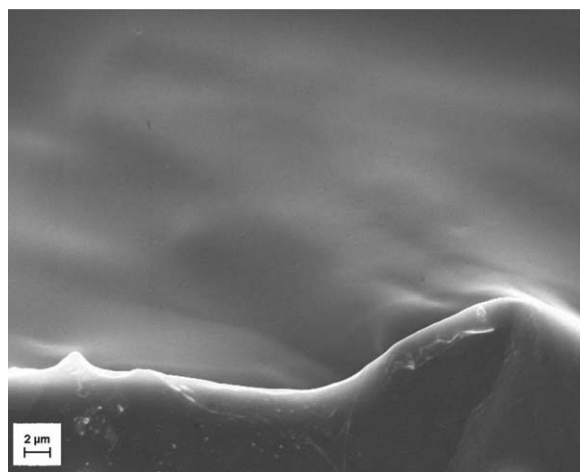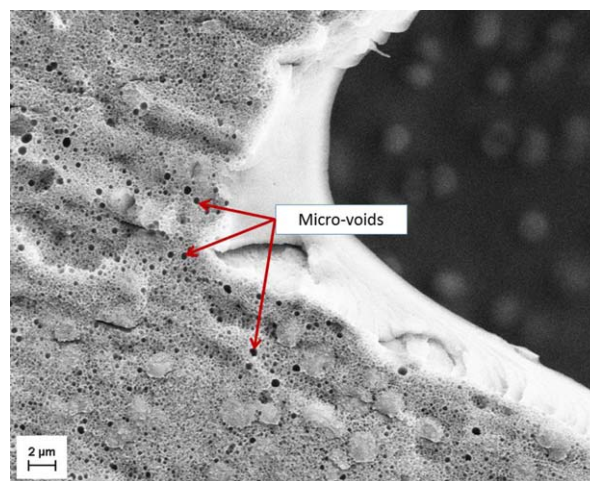| Sample	A_{HCO}	A_{FCO}	R_1	$A_{H\text{-}NH}$	$A_{F\text{-}NH}$	R_2
PU1.3	8.78	3.65	0.71	7.23	0.75	0.91
PU1.5	8.51	3.25	0.72	9.16	0.79	0.92
PU1.7	7.36	2.15	0.77	7.77	0.38	0.95
PU2.0	12.68	3.19	0.80	10.14	0.20	0.98

Table III. The Water Absorption and Working Life of PU Adhesives at Various NCO : OH Ratios

NCO : OH Ratio	Percentage of water absorption, $W\%$		Working life (min)
	25°C	70°C	
1.3	0.27 ± 0.04	5.33 ± 0.12	90
1.5	0.11 ± 0.02	3.99 ± 0.08	10
1.7	0	3.03 ± 0.22	7
2.0	0.07 ± 0.03	3.50 ± 0.13	5.5

Cohesive failure (noted by the blue arrow in the figure) is a failure occurred in the adhesive layer, and the fracture allows the adhesive layer to remain on both sides of the substrate surface. A cohesive failure indicates a stronger bond at the interface, which a desirable condition to attain superior properties in shear strength and delamination resistance of the joint. Adhesive failure (noted by the white arrow in the figure) is a failure occurred at the interfacial bond between the adhesive and the Al surface. Adhesion failures are characterized by the absence of adhesive on one of the bonding surfaces.

Failure occurs along the interface between the adhesive layer and the substrates and is due to hydration of the chemical bonds which form the link between the adhesive and the surface. Bonds between substrates usually fail because the metallic oxide naturally converts to the hydrated form which causes the substrate/adhesive chemical bonds to dissociate leading to disbanding.[24] Figure 7 also shows micrograph of a fractured surface of PU1.7 that the polymer layer is nearly complete remained on the substrate that indicates that the mode of failure found on the fractured surface of PU1.7 is mostly cohesive.

There is no significant change to the failure mode of hydrothermal aged PU adhesive samples at 25°C (Figure 8). PU 1.3, PU1.5, and PU 2.0 show a mixed mode of failure, while PU 1.7 still shows cohesive failure mode as almost entire of the substrate surface is covered with an adhesive layer. Furthermore,
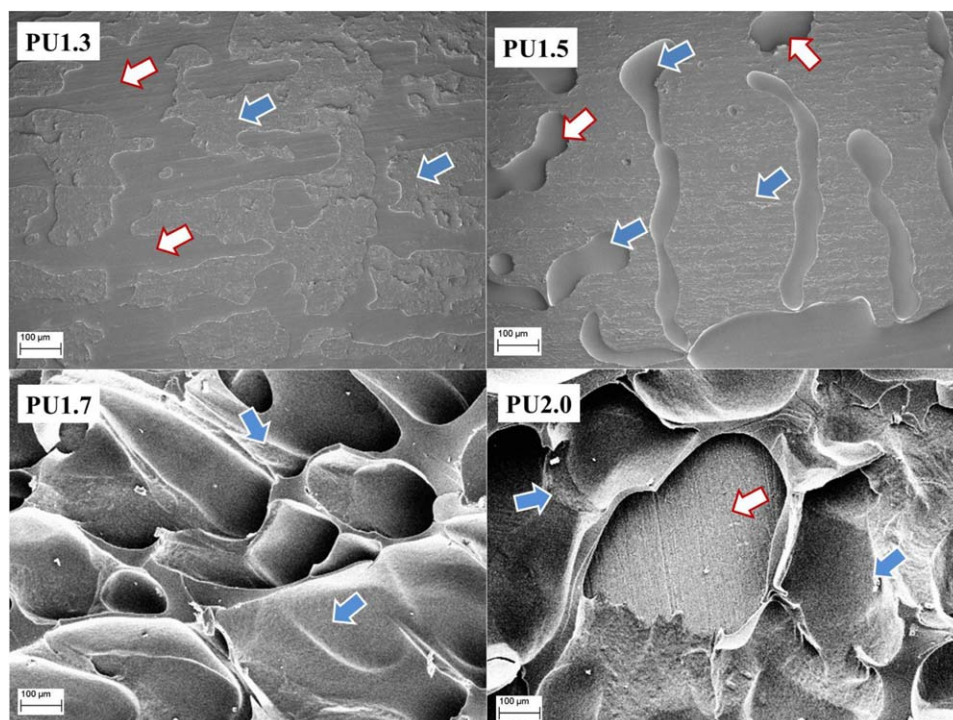

Figure 5. High resolution FESEM micrograph of PU2.0 sample fractured surface (×2000). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the adhesive failure mode region for PU 1.3, PU1.5, and PU 2.0 are larger than the unaged samples.

Increase of ageing temperature will increase the rate of the diffusion of the water to the bondline, and in addition, any chemical degradation of the adhesive, the interface or the metal oxide will be more severe.[25,26] The water retained swells the macromolecular network, which causes tears in the material, together with a selective attack on some functional groups.[27] This damage is permanent and is linked to reaching critical water content and generate sufficiently high tension forces in the polymer to produce a fracture. The hot and humid conditions can change the characteristics of the substrate surface through solvolysis, i.e., by hydration oxide films on the metal substrate.[28,29] In addition, solvolysis produces reaction by-products at the interface that deteriorates the polymer nearby.[30]

A significant change can be observed on the fractured surfaces of PU1.3-PU2.0 (Figure 9) where adhesive failure regions are larger. Figure 9 also shows the effect of swelling and blistering, especially on samples PU1.3 and PU1.5. Meanwhile, the


Figure 4. High resolution FESEM micrograph of PU1.7 sample fractured surface (×2000).
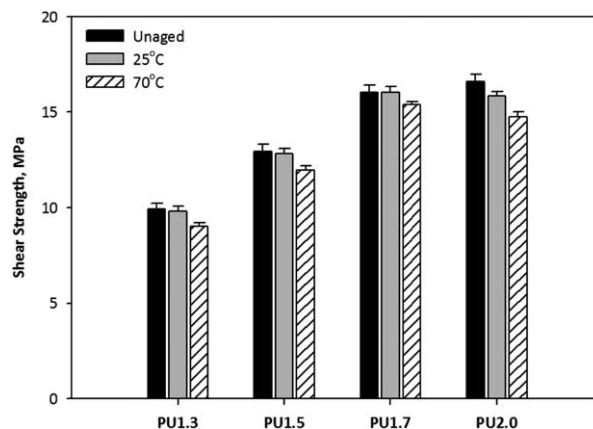
Figure 6. Shear strength of unaged and hydrothermally aged PU adhesive bonding.

Figure 7. Fractured surfaces of unaged PU adhesives bonding (Indicator: white arrow = adhesive failure, blue arrow = cohesive failure). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fractured surface of PU2.0 proves that the adhesive failure caused by the formation of micro-voids at the interface between adhesive and substrate (adhesion zone).

The swelling that occurs due to water molecules bound to the polymer molecule, and it infiltrated into the molecular structure of polymers by hydrogen bonding. There are two ways
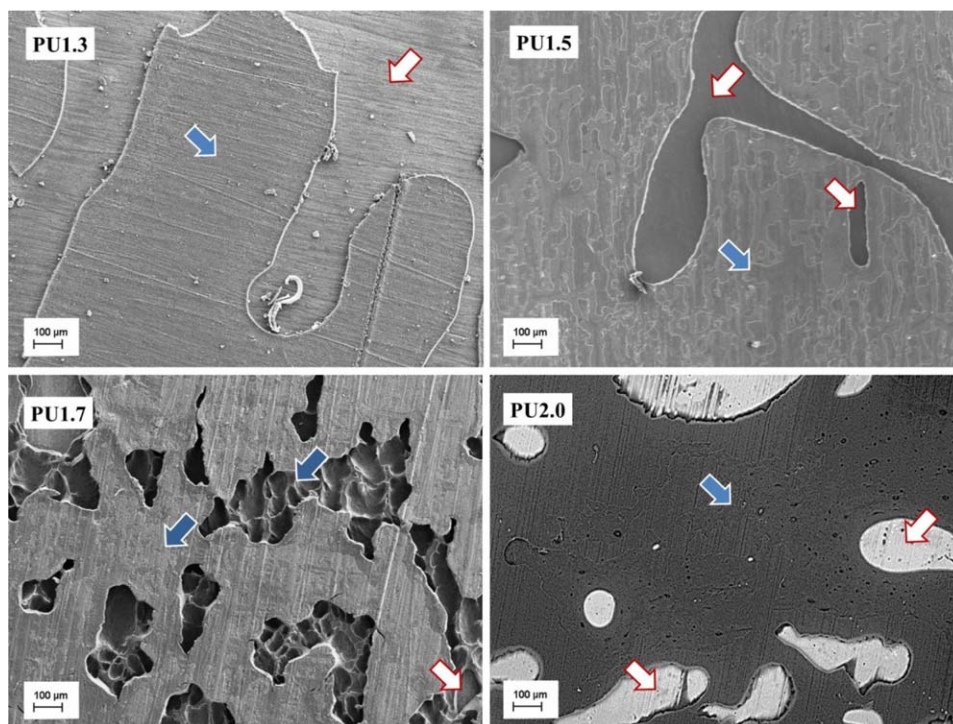
Figure 8. Fractured surfaces of hydrothermally aged PU adhesives bonding at 25°C (Indicator: white arrow = adhesive failure, blue arrow = cohesive failure). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
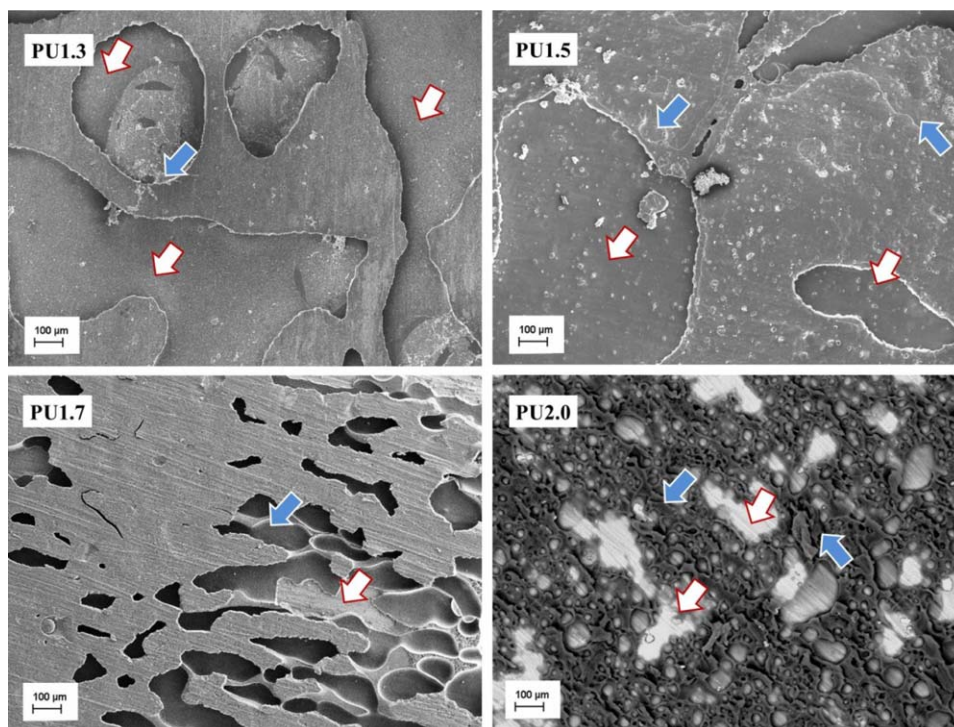
Figure 9. Fractured surfaces of hydrothermally aged PU adhesives bonding at 70°C (Indicator: white arrow = adhesive failure, blue arrow = cohesive failure). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

formation of hydrogen bonding in PU network during the hydrothermal ageing.[31] First, the hydrogen atoms from water molecules are bound with oxygen of urethane and another way is through oxygen atom from water molecules with hydrogen from urethane. Therefore, the water molecules weaken the hydrogen bonding between urethane and thus weaken its adhesion and cohesion strength. This indicates that the water absorption influences the durability of adhesive bonding.

CONCLUSIONS

In dry conditions and at room temperature, higher NCO content revealed a higher crosslink density of PUs, which led to greater lap shear strengths. Nevertheless, the hydrothermal-aged PUs displayed dissimilar trends in their mechanical properties and durability, as well as in their resistance to hydrolysis. The durability and hydrolysis stability of PU adhesives correlated to lower water absorption due to higher NCO content. PU1.7 showed optimal properties in terms of durability and resistance to hydrolysis, whereas PU2.0 revealed deterioration in durability and resistance to hydrolysis due to the presence of greater micro-voids content in the PU2.0 matrix. Besides, the hydrothermal ageing temperatures also influenced the water absorption in the bulk polymer, hence affect the durability of PU adhesives.

ACKNOWLEDGMENTS

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