

Modification of Epoxy Surfaces with Different Polyvinylalcohol Polymers

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SYNOPSIS

An epoxy resin, consisting of diglycidylether of bisphenol A (DGEBA) and methyltetrahydrophthalic anhydride (MTHPA), was cured against peel-plies coated with different poly(vinylalcohol-co-vinylacetate) (PVOH). The epoxy polymer surface was characterized with X-ray photo electron spectroscopy (XPS), contact angle measurements, and scanning electron microscope (SEM). PVOH, which is a water soluble polymer, was detected at the cured epoxy polymer surface with XPS after washing with hot water. The PVOH polymer at the outermost surface has hydroxyl groups, which can react with both the adhesive and the epoxy resin. The modified epoxy composite surfaces were adhesively bonded with a polyurethane and an epoxy adhesive. Improved adhesion was obtained between modified epoxy composite surfaces and different adhesives. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The outermost chemical composition at a polymer surface determines whether the polymer will have good properties with respect to, for example, adhesion, biocompatibility, and friction. One can never expect that the outermost surface composition is the same as the bulk, due to the fact that the surface has been influenced by environments, such as air and molds. The effect of different environments on polymer surfaces has been studied by several authors, who studied both thermosets¹⁻³ and thermoplastics.⁴⁻⁹

An example of an observed effect is when polymers with polar and nonpolar parts are molded against a polar surface or a nonpolar surface, which enriches energetically the most suitable component at the outermost surface.^{1,9} The main reason for this occurrence is that the difference in surface energy, between the surface of the mold and the polymer, should decrease.

During the manufacture of polymer parts using compression molding, release agents or release films are often used for easy removal of the molding from

the mold surface.¹⁰⁻¹² Typically, the molding is prepared in a mold that is coated with an oil, waxy, fluoroorganic, or silicone release agent. The release agents must be removed by solvent wash or by mechanical methods, such as grinding, because they contaminate the polymer surface. In adhesion, it is important to avoid these contaminations, which act as weak boundary layers that cause a decrease in adhesion strength.

Thermosetting composite materials are often protected with peel-plies. These are used for at least two reasons. One reason is to protect the surface from release agents prior to adhesive bonding and the other reason is to increase the overall bonding area. Investigations show that even the peel-plies can contaminate the composite surface.¹³⁻¹⁵ To obtain reliable adhesive joints, this contamination must be removed in some cases, which often is done by mechanical methods, such as abrasive blasting with sand.¹⁴

Every mold contaminates the surface, but the effect on adhesion can be different and depends on the nature of the contaminant. Using the contamination from the mold surface for a deliberate modification of the surface is an interesting way to improve the surface properties. Several steps can be saved if the protecting peel-ply can modify the polymer surface to improve the adhesion.

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The aim of this work is to use the surface of the mold to modify the polymer surface. If the mold is coated with a water soluble polymer, and a resin such as epoxy is molded in this mold, the water soluble polymer will contaminate the cured epoxy surface. An excess of nonbonded water-soluble polymer can be dissolved with water. If there is any remaining polymer, bonded at the epoxy surface, it can contribute to increased wettability and adhesion, provided it contains suitable functional groups. In this work, we have used polyvinyl alcohol, since it is water soluble and contains hydroxyl groups. XPS and contact angle measurements were used to characterize the modified polymer surfaces and different adhesives were used to determine if the modification increased the adhesive strength.

EXPERIMENTAL

Materials and Methods

The epoxy resin in the epoxy-glassfiber composite consisted of diglycidylether of bisphenol A (DGEBA) (LY556) and methyltetrahydrophthalic anhydride (MTHPA) (HY917), and tertiary amine (DY062) as an accelerator, which all were supplied from Ciba-Geigy. The ratio between the components DGEBA and MTHPA was 100 : 80 by weight and the accelerator added was 0.25% of the total weight.

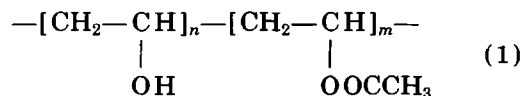
The glass fiber fabric, supplied by Alströms Glassfiber AB, was 0.5 mm thick and the fibers were oriented in one direction. The glass fiber was wetted with epoxy resin, with the hand lay up method, and the composite was cured in an aluminum frame (200 × 200 mm) at 150°C for 1 h in a hydraulic press.

The mold surface consisted of a polyamide 6.6 peel-ply, which was impregnated with water-soluble polymers. Solutions of 5% by weight of water-soluble polymers were used to impregnate the peel-ply. The impregnation was dried for 1 h at 80°C to form a dry coating.

As reference mold surfaces, two commercial peel-pplies (Burlease) were used: super blue release (SBR) and Natural (NAT), from Burlington Industries (United Kingdom). SBR is a silicon-modified polyamide and NAT is a polyamide peel-ply. An epoxy surface, obtained by grinding with sandpaper, was also used as reference.

After curing against the different water soluble polymers, the epoxy surfaces were washed with 95°C water to remove nonbonded and soluble excess of the water soluble polymer. This was done for 1 h with an exchange of water every 15 min. The overall procedure is presented in Figure 1. Poly-

(vinylalcohol-*co*-vinylacetate) (PVOH) [eq. (1)] of different molecular weights, $M_w = 15,000$ – $224,000$, and different content of hydroxyl groups, was used as water soluble polymer.



The washed epoxy surfaces were adhesively bonded with both a two-component polyurethane adhesive (Casco 1897/976) and a two-component epoxy adhesive (Ciba Geigy AW2104/HW2934). The adhesive joints were of the double overlap type with an overlap of 12.5 mm and a width of 25 mm. The bondline thickness was controlled with a stainless steel thread, which was 0.1 mm thick (Fig. 2). The lap shear strength of the double overlap joints was measured with an Instron 1193, at 10 mm/min, and a load cell of 20 KN. The joints were tested one week after assembling. The lap shear strength given is an average of eight samples.

XPS

The polymer surfaces were analysed with a Hewlett Packard 5950 ESCA spectrometer, with a monochromatic Al(K_α) X-ray source, in an ultra high vacuum (background pressure 10^{-8} – 10^{-9} torr). The escaping electrons were counted as a function of their kinetic energy. The take off angle was 45° and the analyzed area was 1 × 5 mm with an information depth of 50–70 Å. The build-up of positive charge (4–5 eV) on the polymer surfaces was neutralized by electrons. A graphics terminal was used for the curve fit procedure with Gaussian peaks and a linear background. Scofield's cross sections¹⁶ were used in the calculations to determine the relative amount of the elements.

Contact Angle Measurement

Contact angles of water and methylene iodide on polymeric surfaces were measured using a goniometer (NRL Contact Angle Goniometer, Model A-100, Rame'–Hart, Inc.). The standard deviation of ten measurements (one measurement of each side of five drops placed randomly across the surface) was between $\pm 1^\circ$ and $\pm 3^\circ$.

SEM

A JEOL JSM-35 scanning electron microscope (SEM) was used to detect whether there were any

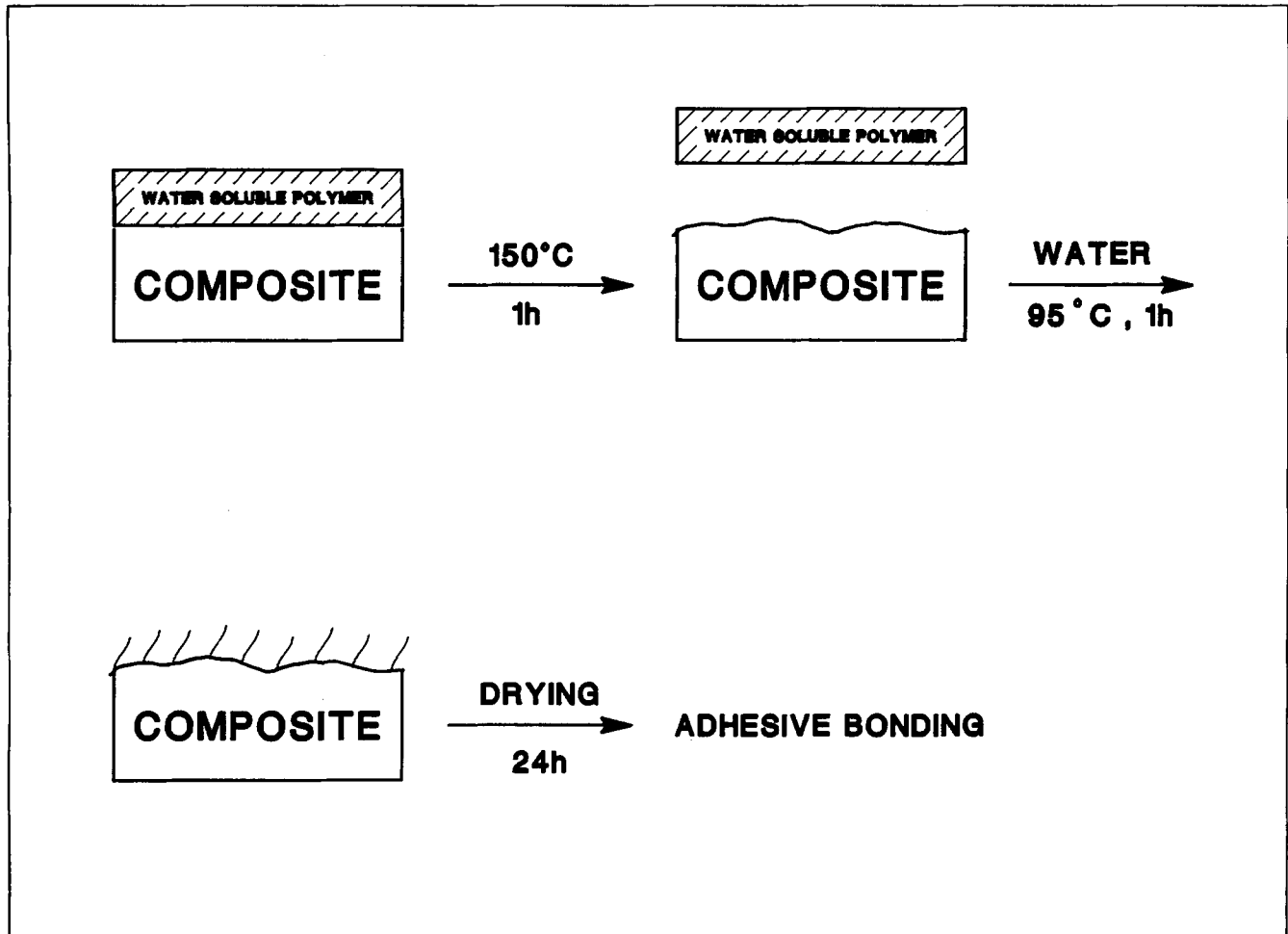


Figure 1 The procedure used to modify the epoxy polymer surface.

residues from the peel-ply at the epoxy surfaces. The specimens were coated with gold to prevent electrical charging.

RESULTS AND DISCUSSION

Poly(vinyl alcohol) (PVOH) is, in fact, a copolymer made by hydrolysis of the acetate groups in poly(vinyl acetate) to hydroxyl groups. The name PVOH is often used as an abbreviation for poly(vinylalcohol-*co*-vinylacetate). The extent of hydrolysis of the copolymers used is presented in Table I. The solubility properties in water¹⁷ depends on the extent of hydrolysis. A high content of hydroxyl groups decreases the solubility in water, due to increased hydrogen bonding between the polymer molecules.

When water solutions of PVOH are dried in air, the outermost chemical composition is different from the bulk.¹⁸ The less polar acetate group was found to be in excess at the outermost surface, as compared to the bulk content. It is important to know that the PVOH-coated peel-ply surfaces have an increased content of acetate groups, which makes the surface more hydrophobic, as compared to the bulk.

The contact angle measurements of the PVOH films in Table II show that the surface energy decreases with increasing molecular weight and the same degree of hydrolysis. This can be an effect of the decreased solubility with increased molecular weight. The values were taken immediately after positioning the drop on the PVOH film. Water solubilizes the polymer and swells it, which generates a completely different surface. This makes the standard deviation too large.

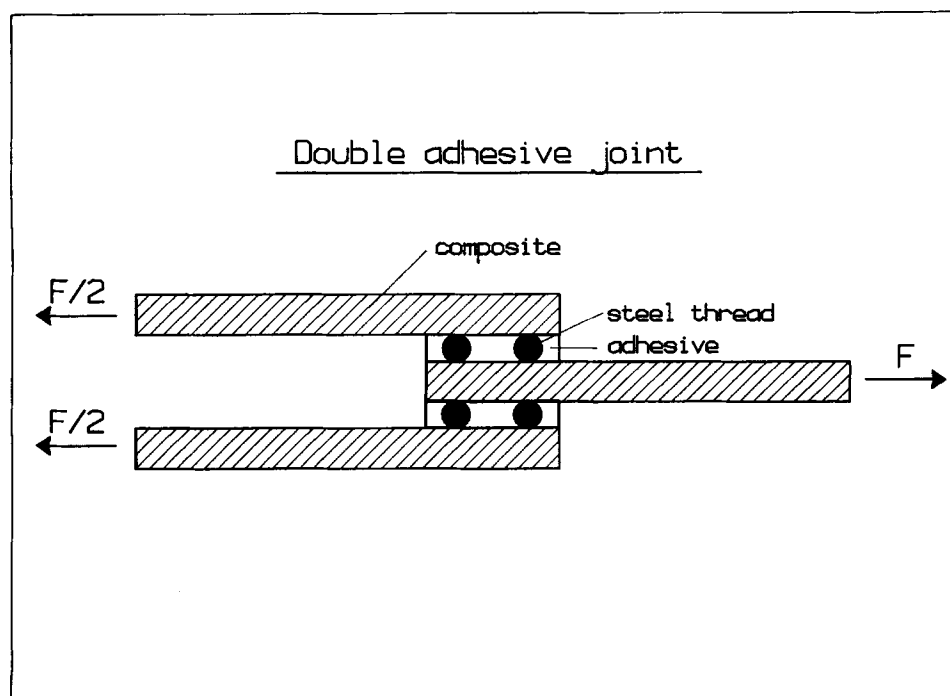


Figure 2 A model of the double overlap adhesive joint used in this measurement.

The Reference Surfaces

Two different peel-plies, a polyamide 6.6 and a silicon modified polyamide, were used as reference surfaces to compare with the peel-plies that were modified with polyvinyl alcohol. The third reference surface was an epoxy surface, obtained by grinding with sandpaper, which simulates the bulk.

One of the reasons for using a peel-ply is to increase the surface area. Figure 3 presents SEM micrographs of epoxy surfaces molded to different peel-plies. It is obvious that the pattern is transferred to the surface of the molded part. It is important to note that no differences can be seen for the PVOH modified surfaces before and after washing and that no fiber fragments are seen.

Molding against the peel-plies caused contamination on the epoxy polymer surface. Figure 4 presents the XPS survey spectra for an epoxy surface that was molded against the different peel-plies. Silicon and nitrogen was found at the epoxy surface as contaminants, which indicates that polyamide is transferred to the epoxy surface. The elemental composition of the different surfaces is presented in Table III.

The level of oxygen content is higher at the epoxy surfaces that were molded against the PVOH modified peel-plies as compared to the bulk oxygen content. This indicates that the polyvinyl alcohol polymer remains at the epoxy surface. The oxygen content is, in fact, the same as for the pure PVOH films.¹⁹ Furthermore, the contact angle measure-

Table I Comparison of Bulk Content and the Found Surface Content Measured with NMR and XPS

Polymer	Supplier	Hydroxyl Content (mol %)		M_w (g/mol)	Supplier
		NMR	XPS/ $\theta = 45^\circ$ /AIR ^a		
PVOH-15	86	86	57	15,000	Fluka
PVOH-45	86	86	62	45,000	Fluka
PVOH-100	86	86	69	100,000	Fluka
PVOH-224 ^b	99	98	74	224,000	Hoescht

^a Values from Ref. 19.

^b Mowiol 66-100.

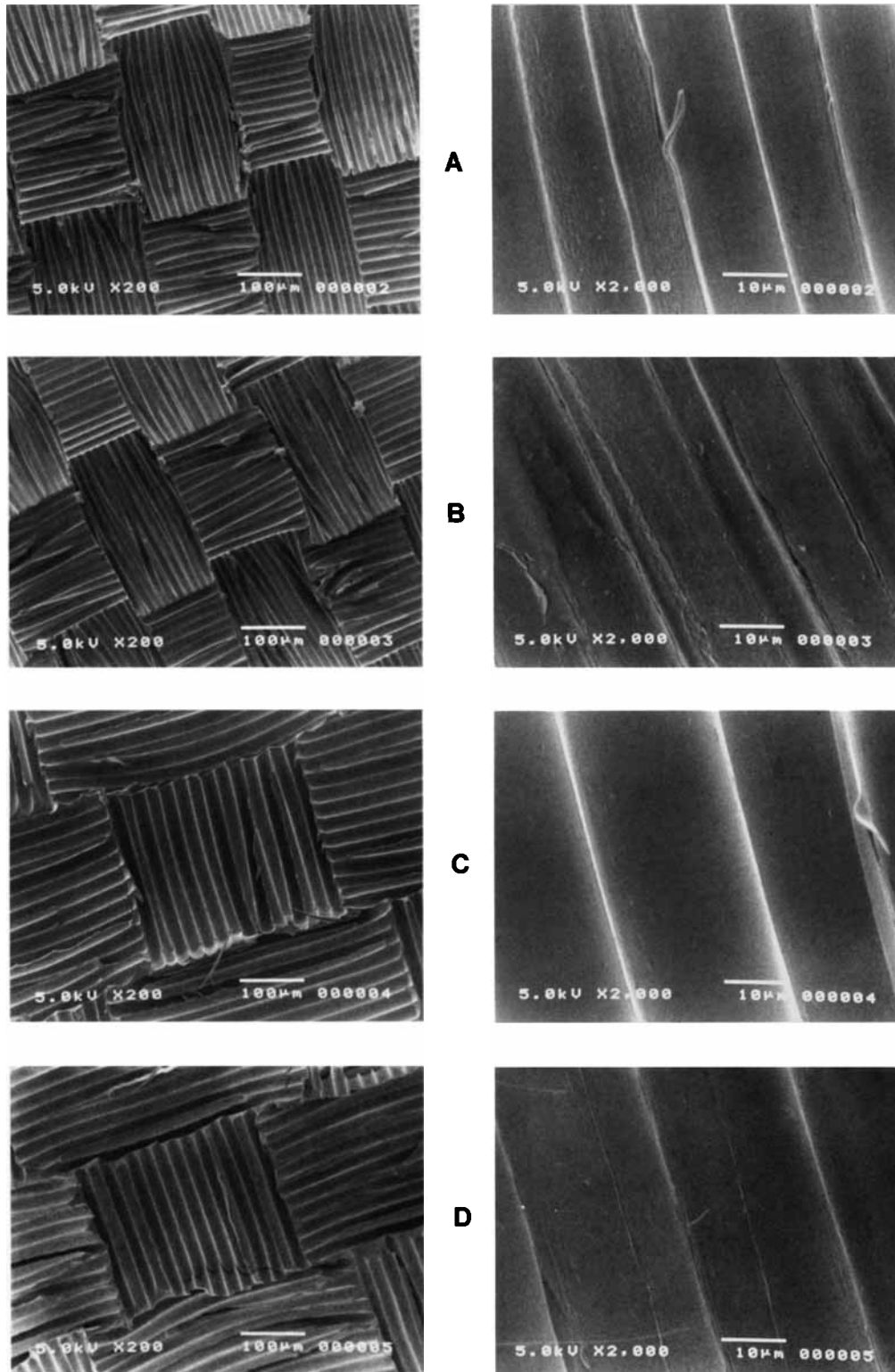


Figure 3 SEM micrographs of epoxy surfaces molded to different peel-plies (A) polyamide, (B) silicon-modified polyamide, (C) PVOH-49,000-coated polyamide (unwashed epoxy surface), and (D) PVOH-49,000-coated polyamide (washed epoxy surface).

Table II Advancing Contact Angle Measurements of PVOH Films and Washed Epoxy Surfaces^a

Polymer	PVOH-Film		Epoxy Surface Washed	
	θ_w/θ_{MI}	γ_{tot}^b	θ_w/θ_{MI}	γ_{tot}
PVOH/15,000	62/42	48.1	62/36	49.7
PVOH/49,000	79/41	41.5	62/38	49.1
PVOH/100,000	91/39	40.7	62/42	48.1
PVOH/224,000	63/38	48.6	63/33	50.0

^a Water (*W*) and methylene iodide (*MI*) were used as probing liquids.

^b Calculated according to the harmonic equation.¹⁸

ments show similar values for the washed epoxy surfaces and the PVOH-film, Table II also indicates a similar composition.

The anhydride and the epoxy groups in the epoxy resin can react with the hydroxyl groups in the PVOH. These reactions can explain why PVOH remains at the epoxy surface after washing. Both XPS and contact angle measurements indicate that all the washed epoxy surfaces have similar compositions at their outermost surfaces.

The Adhesion Strength

The adhesive properties were evaluated with an epoxy and a polyurethane adhesive. The adhesion strength, measured for the epoxy surfaces modified with the different PVOH polymers, are presented in Figure 5. For comparison, the adhesion strength for the reference surfaces are shown in Figure 6. The low adhesion strength for the reference peel-pplies is probably due to the contaminations from the

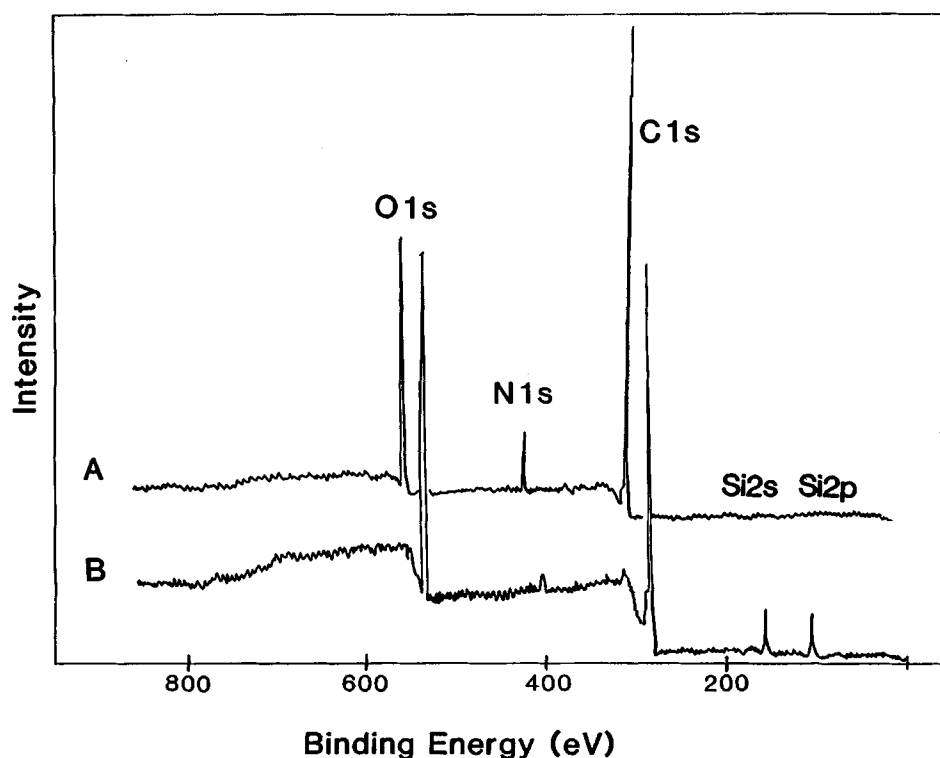


Figure 4 XPS survey spectra of epoxy surfaces, molded to polyamide (A) and silicon-modified polyamide (B) peel-pplies.

Table III Atomic Composition Measured with XPS of the Epoxy Polymer Surface, Molded Against Different Peel-Plies

Peel-Ply	C	O	N	Si
Polyamide	77	17	6	—
Silicon/polyamide	70	21	2	7
Ground/bulk	80	20	—	—
PVOH-15,000	69	31	—	—
PVOH-49,000	69	31	—	—
PVOH-100,000	69	31	—	—
PVOH-224,000	69	31	—	—

peel-plies found at the epoxy surface. Cohesive failure within the adhesive was only obtained for bulk and PVOH surfaces bonded with PUR.

Improved adhesion was found for every PVOH polymer, as compared to both grinded surface and pure polyamide peel-ply. There are also differences between the adhesives and the different PVOH polymers. The epoxy adhesive was found to have lower adhesion strength, as compared to the polyurethane adhesive.

The ground surface, which represents the bulk, has reactive functional groups present at the outermost surface.¹ The PVOH polymer has more reactive functional groups and a higher surface energy, which produces a surface with increased wettability and more possibilities for the creation of chemical bonds. This can be the reason for the improved adhesion strength between the modified surfaces and the adhesives.

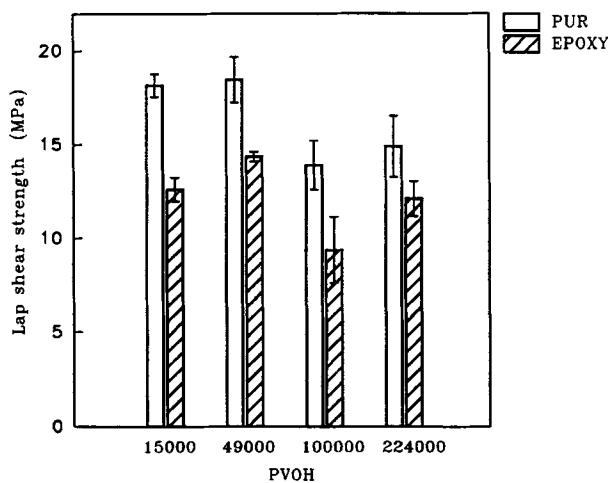


Figure 5 The lap shear strength of the different PVOH polymers used.

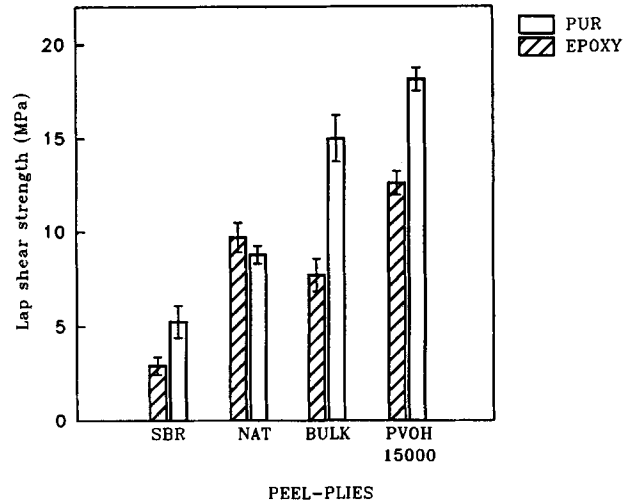


Figure 6 The lap shear strength for different reference surfaces.

As can be seen in Figure 5, the adhesive strength is highest for the lower molecular weight polyvinyl alcohol polymers. Decreased solubility in water, with increased molecular weight, can be an explanation for the difference in adhesive strength, since non-bonded PVOH chains may still remain at the surface after washing. Another explanation for the difference in adhesive strength could be the miscibility between the PVOH and the epoxy resin. The miscibility increases with decreased molecular weight, which produces better anchoring of the PVOH that is left at the surface.

The epoxy adhesive shows generally a lower level of adhesive strength. A reason for this can be the lower reactivity of the epoxy groups towards the hydroxyl groups of the PVOH, as compared to the corresponding reaction involving the isocyanate groups of PUR. Another important factor is that the epoxy is cured with amines, which perhaps do not leave many epoxy groups that can react at the surface.

The result shows that it is possible to improve the adhesion strength by using an opposite protective peel-ply. The possibilities do not end with this type of polymer, but perhaps a water soluble polymer with amines would be effective.

CONCLUSIONS

The adhesion was improved between the adhesives used and the PVOH modified surfaces were compared to different reference surfaces. XPS mea-

surements detected PVOH at the epoxy polymer surface and different contamination residues from the uncoated peel-ply. The best results were obtained with polyvinyl alcohol polymers, with lower molecular weight, which could be due to increased solubility in water.

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