

EFFECTS OF RELATIVE HUMIDITY AND SHELF-LIFE ON SELECTED PROPERTIES OF POLYVINYL ACETATE ADHESIVE FILMS¹

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ABSTRACT

The effects of various relative humidities and shelf-lives on the tensile and thermal properties of a commercial polyvinyl acetate copolymer emulsion (PVAC) adhesive are reported. Adhesive-free films, from both crosslinkable and uncrosslinkable resins at three different shelf-life periods, were formed in an environmental chamber (72% relative humidity). After curing, specimens were cut from the films and divided into experimental units; and each unit was conditioned at a different relative humidity (0, 40, 60, and 90%). Tensile and differential scanning calorimetry tests were conducted after the films reached equilibrium at the various relative humidities. Tensile testing results indicate that at relative humidities greater than 40% the tensile strength and modulus of elasticity of both uncrosslinked and crosslinked films decrease. Shelf-life periods of 1.5, 2.5, and 3.5 months had relatively little effect on the tensile strength and modulus of elasticity values of either crosslinked or uncrosslinked PVAC films as compared to the effects of relative humidity. Regression analysis established that the mechanical properties varied mainly as a function of relative humidity. Differential scanning calorimetry specimens were cut from the same sheets of free film as the tensile specimens. Crosslinked and uncrosslinked specimens from an initial shelf-life period of 1.5 months were tested to determine the effects of relative humidities on the calorimetric properties of the films. The results indicate that relative humidity, especially at levels greater than 40%, affects some of the calorific values obtained from the films.

Keywords: Adhesives, polyvinyl acetate, tensile properties, differential scanning calorimeter, relative humidities, shelf-life, films.

INTRODUCTION

The American Society for Testing and Materials, British Standards, and other organizations have over the years adopted various standard test methods for evaluating polymers both by themselves or as a composite. The standard wood block shear test and other joint tests are implemented to reveal the mechanical properties of synthetic or natural polymeric materials adhered by synthetic or

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naturally occurring polymeric adhesives. Generally these test methods work well, but the procedures limit the range of variables that are tested.

Testing the shear strength properties of adhesives used in bonding wood usually requires the specimens to be conditioned at a particular relative humidity and temperature prior to testing. The results of the test are the strength properties of bonded wood at the standard test environmental conditions. If the wood fails before either the adhesive (cohesive strength) or the interface between the adhesive and wood, then the ultimate strength of either the adhesive itself or adhesive bond is not reached.

Effects of various relative humidities on the properties of adhesives are of interest in understanding bonded wood failures, particularly when the bonded wood is subjected to changing environmental conditions. Quantification of environmental effects will aid in the utilization of adhesives.

Blends of polyvinyl alcohol (PVA) with polyvinyl acetate copolymer (PVAC) emulsions, when used as wood bonding adhesives, provide excellent bond strength, fast-setting colorless glueline, and ease of application. Despite these advantages, the adhesive bonds derived from conventional vinyl acetate homo or copolymer emulsions as well as vinyl acetate homo or copolymer emulsions that contain PVA exhibit poor water resistance. According to patents (e.g., Armour *et al.* 1971) issued depicting the PVAC adhesive used in this study, these aforementioned difficulties would be substantially overcome if acidic metal salt curing agents were used. This point was demonstrated by examples contained in patents issued to several resin manufacturers (e.g., Armour *et al.* 1971).

In related research, Galperin and Arnheim (1967) evaluated the effects of various relative humidities on the tensile properties of TiO_2 filled and unfilled polyvinyl acetate. It should be noted that the 2–4-mm films tested were made from solutions of polyvinyl acetate in 2-butanone, which is not an emulsion. The result of this study was a proposed mechanism stating that the packing of polymer chains was altered by water, perhaps affecting the movement of acetate side groups, and thereby changing intermolecular forces with resultant changes in tensile properties. Also, Simpson and Soper (1968) investigated the stress-strain behavior of four adhesive films used with wood. In that study they determined that adhesive cure time did not have a measurable effect on the stress-strain behavior.

In addition to mechanical testing, thermal analysis of polymers is another method that can be used either to investigate polymer thermal degradation or for comparing polymer thermograms for polymers possibly degraded by pretreatments or previous environmental conditions. Thermograms from a differential scanning calorimeter (DSC) are useful in determining molecular information about polymers. The DSC can be used to determine total heat in cal/g of an exo- or endotherm and the specific temperature at which this event occurs. Interpretation of these values may be of assistance in understanding the mechanism of a specific degradation process.

The purpose of this study is to report on the effects of relative humidity and shelf-life on tensile properties of a commercial polyvinyl acetate copolymer emulsion (PVAC) adhesive. In addition, differential scanning calorimetry tests were conducted on specimens to observe whether any changes in the thermograms occurred in the adhesive polymer because of exposure to various relative humidities.

EXPERIMENTAL PROCEDURE

The adhesive resin used in this study was a single batch of aqueous vinyl acetate copolymer emulsion containing polyvinyl alcohol as a protective hydrocolloid. The curing agent or crosslinking agent was an acidic metal salt (3% by weight). Crosslinked and uncrosslinked adhesive-free films were made at three shelf-life periods (1.5, 2.5, and 3.5 months). These films were formed in an environmental chamber at a relative humidity of 72%. After curing of the films from each shelf-life period for 24 h (films reached mass loss equilibrium), specimens were cut and divided into four experimental units (Cowan 1977). Each experimental unit was conditioned at a different relative humidity (0, 40, 60, and 90%). Tensile and differential scanning calorimetry tests were conducted after the films reached equilibrium at the various relative humidities.

Specimen preparation

Film preparation was made on a thin layer chromatography apparatus equipped with a stainless steel doktor blade and coated glass plates (Cowan 1977). This apparatus consistently produced high quality thin films. The process of forming thin films consisted of initially washing the glass plates in hot detergent, followed by acid bath washing and forced air oven-drying. Each plate was polished with a release agent and placed in a forced air oven, at 105 C for 15 min, to remove any volatiles. The chromatography apparatus was equipped with a locking side panel that permitted the operator to accurately install five coated plates simultaneously. A small four-sided hollow spreader box with a vertically adjustable doktor blade was adjusted to a thickness of 0.072 mm by use of a feeler gauge. The adhesive was poured into the spreader box and the films were formed with a single uniform stroke. The adhesive coated plates were kept in the 72% relative humidity room for 24 h before the test specimens were cut from the films. It should be noted that at relative humidity conditions of less than 72%, the films tended to dry too rapidly, inducing hole formation, especially if a catalyst was used.

The films were easily peeled from the glass plates, coated with a release agent, and placed in a jig, that produced 5 mm × 15 mm rectangles (Cowan 1977). Specimen thickness at ten points across the length of the specimens was measured using a linear transducer, and the specimens used in the mechanical testing equipment had a standard specimen thickness of 0.686 ± 0.0254 mm.

The specimens were suspended in chambers containing relative humidities of 0, 40, 60, and 90%. The chambers contained a solution of glycerin and water yielding a specific predetermined relative humidity (Newman 1968). After exposures of not less than 48 h, the specimens were ready to be tested. The exposure time required to reach equilibrium was established by equilibrium mass determinations during conditioning at the various relative humidities (Cowan 1977).

Tensile testing

The tensile testing system for obtaining the load-elongation curves for thin free-film consisted of zero-span grips (TAPPI Standard T 231 su-70), an environmental control system, and a Tinius Olsen Universal testing machine. The zero-span

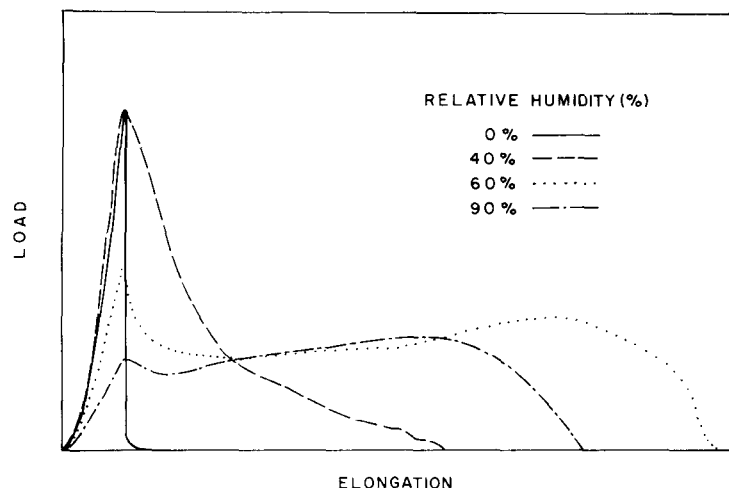


FIG. 1. Typical load elongation curves for crosslinked and uncrosslinked PVAC films conditioned and tested at selected relative humidities.

grips were gapped at 0.1524 mm via a microscope cover slide slipped between the grips prior to each run.

Load-elongation data were obtained with a crosshead speed of 0.127 cm/min. Modulus was calculated by dividing the load per original cross-sectional area by the change in elongation per original length. Tensile strength was determined by the maximum load divided by the original cross-sectional area.

The zero-span grips were mounted to the testing machine and were contained in a polymethylmethacrylate testing chamber. This chamber was used to control the relative humidity environment around the specimens during testing (Cowan 1977). Internal chamber temperature was thermostatically controlled by the external room, which was maintained at 22.2 C. Internal temperature conditions were periodically monitored by a thermocouple probe and mercury thermometer. The relative humidity within the chamber was continuously monitored and recorded during the testing procedures by narrow-band hygrosensors coupled to an electronic hygrometer and a strip chart recorder.

Aqueous solutions of glycerin were prepared to maintain chamber relative humidity conditions of 40, 60, and 90%. Air was bubbled through glycerol at low pressure and then into the chamber. In order to obtain an internal chamber condition of 0% relative humidity, the chamber air had to be dried by bubbling it through 96% H_2SO_4 followed by a series of dryers containing anhydrous calcium sulfate. This procedure produced a relative humidity that was consistently less than 3% of full scale on the low relative humidity narrow-band hygrosensor. Thus the relative humidity was essentially a nominal 0%.

Differential scanning calorimetry (DSC) testing

Specimens tested in the DSC were obtained from the same sheet of film as the tensile specimens. A Perkin Elmer DSC-I thermal analyzer with a heating rate of 10 C per minute was used to obtain a continuous differential thermogram containing exo- and endotherm peaks and temperature changes. The specimen weight

TABLE 1. *Tensile properties of polyvinyl acetate copolymer crosslinked and uncrosslinked films.*

Shelf-life (months)	Relative humidity (%)	TENSILE STRENGTH			MODULUS OF ELASTICITY		
		No. of specimens	Mean (psi)*	Coefficient of variation (%)	No. of specimens	Mean (psi)*	Coefficient of variation (%)
CROSSLINKED							
1.5	0	10	5,212	15.3	10	6,027	33.7
	40	12	4,831	24.2	12	6,738	20.8
	60	10	3,585	27.9	10	2,630	28.5
	90	8	1,659	45.9	8	1,123	35.9
2.5	0	7	3,342	19.4	7	6,103	20.1
	40	10	3,840	21.0	10	5,759	26.1
	60	9	4,319	37.3	9	2,244	40.3
	90	6	175	91.9	6	47	93.2
3.5	0	9	4,739	35.8	9	4,782	30.6
	40	6	5,637	19.7	6	6,378	11.2
	60	10	3,534	16.4	10	3,452	11.3
	90	8	258	44.9	8	532	36.2
UNCROSSLINKED							
1.5	0	9	3,786	23.6	9	4,224	32.1
	40	11	3,791	32.6	11	3,762	38.2
	60	11	3,814	23.7	11	2,187	34.9
	90	7	670	30.6	7	95	27.2
2.5	0	10	3,636	23.1	10	5,556	19.3
	40	10	4,145	23.7	10	5,047	13.0
	60	8	1,348	38.7	8	434	50.8
	90	6	186	19.1	6	34	16.9
3.5	0	8	4,164	32.6	8	5,388	42.3
	40	9	4,040	28.1	9	3,687	27.9
	60	5	5,340	14.7	5	3,374	20.9
	90	**	**	**	**	**	**

* 1 psi = 6.895 kPa.

** Specimens could not be tested.

was approximately 2 mg. In differential scanning calorimetry, the variation in power input to maintain an equal temperature level between a reference pan and the sample pan during a transition is measured.

Specimens from shelf-life of 1.5 months, crosslinked and uncrosslinked, at four relative humidities were chosen for analysis because the shelf-life periods tested in this study did not have any effect on the tensile properties. The areas under exo- and endotherm peaks were measured with a compensating planimeter. The temperature was recorded at the beginning of the endotherm and at the apex of the exotherm. The area measurement was converted to calories per gram of specimen weight (Cowan 1977).

RESULTS AND DISCUSSION

Mechanical properties

Load-elongation curves (typical curves are shown in Fig. 1) for both the crosslinked and uncrosslinked PVAC films changed as the relative humidity increased from 0 to 90%. Generally, as the relative humidity increased, the tensile properties decreased and the elongation at failure increased. Table 1 lists the tensile prop-

TABLE 2. Summary table of multiple regression analysis.*

TENSILE STRENGTH		MODULUS OF ELASTICITY	
Regression equation	R ² %	Regression equation	R ² %
CROSSLINKED			
Y = 3,293 + 1,063 X1 + 1,335 X2 + 202.8 X3 + 490.0 X4 - 587.0 X5	69.6	Y = 3,790 + 1,826 X1 + 2,521 X2 - 996.2 X3	77.5
UNCROSSLINKED			
Y = 2,909.0 + 953.1 X1 + 1,083.0 X2 + 587.4 X3 + 106.3 X4 - 583.4 X5 - 182.3 X6 + 357.5 X7 - 307.2 X8 + 736.1 X9 + 211.4 X10 - 1,578.0 X11	70.4	Y = 2,751.0 + 229.0 X1 + 1,404.0 X2 - 810.0 X3 - 638.0 X6 - 492.9 X7 - 239.4 X8 - 878.7 X9 + 399.4 X10 - 1,524.0 X11	74.9

* Key to variables: Significant at 5% level.

$$X1 = \begin{bmatrix} 1 = 0\% \text{ RH} \\ 0 = 40, 60\% \text{ RH} \\ -1 = 90\% \text{ RH} \end{bmatrix} \quad X2 = \begin{bmatrix} 1 = 40\% \text{ RH} \\ 0 = 0, 60\% \text{ RH} \\ -1 = 90\% \text{ RH} \end{bmatrix} \quad X3 = \begin{bmatrix} 1 = 60\% \text{ RH} \\ 0 = 0, 40\% \text{ RH} \\ -1 = 90\% \text{ RH} \end{bmatrix}$$

$$X4 = \begin{bmatrix} 1 = \text{shelf-life } 1.5 \\ 0 = \text{shelf-life } 2.5 \\ -1 = \text{shelf-life } 3.5 \end{bmatrix} \quad X5 = \begin{bmatrix} 1 = \text{shelf-life } 2.5 \\ 0 = \text{shelf-life } 1.5 \\ -1 = \text{shelf-life } 3.5 \end{bmatrix} \quad X6 \text{ through } X11 = \begin{bmatrix} \text{Interaction} \\ \text{Terms} \end{bmatrix}$$

$$\begin{aligned} X6 &= (X1)(X4) \\ X7 &= (X1)(X5) \\ X8 &= (X2)(X4) \\ X9 &= (X2)(X5) \\ X10 &= (X3)(X4) \\ X11 &= (X3)(X5) \end{aligned}$$

erties data and related statistics for various shelf-lives and relative humidities. Multiple regression analyses using indicator variables (Neter and Wasserman 1974) were performed on the data in Table 1 and a summary of these analyses are given in Table 2. All equations are significant at the 5% level.

The crosslinked modulus of elasticity equation that best described the data was determined by analysis of variance. The analysis indicated that only relative humidity contributed significantly to the variation in modulus of elasticity. In the uncrosslinked modulus of elasticity equation, relative humidity was again significant and produced an R² value of 66.2%. In addition, relative humidity shelf-life interactions contributed an additional 8.7% to the R² value and was highly significant; thus it was included in the prediction equation.

In the crosslinked tensile strength equation, the presence or absence of the indicator variable for shelf-life contributed very little to the R² values although it was significant at the 5% level. Relative humidity, which was highly significant at the 5% level, contributed to the major portion of the R² values. Several interaction terms contributed very little to the R² value and were not included in the prediction equation. The resultant regression equation contained parameters for relative humidity and shelf-life. All parameters in the uncrosslinked tensile strength equation—i.e., shelf-life, relative humidity, and relative humidity shelf-life interaction terms—were found to be highly significant and are included in the equation.

Differential scanning calorimetry (DSC) data

The DSC can be used to investigate polymer thermal degradation or for comparing polymer thermograms of polymers possibly degraded by pretreatments or

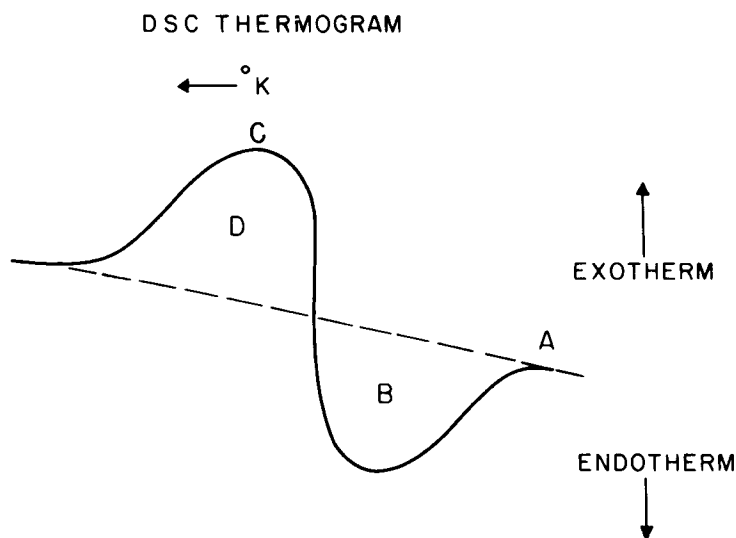


Fig. 2. Typical DSC thermogram for PVAC films.

previous environmental conditions. In this study, the DSC was used to investigate whether the relative humidity treatments altered the polymer thermogram. Alteration of a thermogram may indicate possible polymer degradation or changes in the polymer configuration. Specifically, decreases in endotherm energy as a function of relative humidity levels indicate that less energy is required for polymer bond degradation prior to the release of energy in the exothermic reaction. This implies that the polymer has been altered prior to thermal analysis by the relative humidity treatments.

Data from the DSC thermograms are given in Table 3, and Fig. 2 is a typical DSC thermogram for PVAC films. The endotherm (B in Fig. 2) and exotherm (D in Fig. 2) peak areas (cal/g), along with the beginning endotherm peak temperature (A in Fig. 2) and maximum exotherm peak temperature (C in Fig. 2), are listed in Table 3 with the various relative humidity treatments.

As relative humidity increases, the area under endothermic peaks of both crosslinked and uncrosslinked films decreases. The endotherm peak areas for crosslinked specimens were larger at corresponding relative humidities than for the uncrosslinked specimens, indicating that more polymer bonds are present in the crosslinked as compared to uncrosslinked specimens. Endotherm temperature taken at the beginning of the peak for both crosslinked and uncrosslinked specimens decreases slightly at relative humidities ranging from 0 to 60%. As the relative humidity rises above 60%, the endotherm temperature displays a larger decrease in values for uncrosslinked than for crosslinked specimens. A decrease in the endotherm area as relative humidity increases implies a possible alteration of the polymer configuration and/or polymer degradation due to the relative humidity treatment. Less endotherm energy is required to separate the polymer chains, depolymerize, and/or degrade the remaining polymer chain as prior relative humidity treatment levels increase. The exact degradation mechanism is not

TABLE 3. *Differential scanning calorimetry data.*

Relative humidity %	ENDOTHERM*		EXOTHERM*	
	Cal/g	Beginning peak temp. °K	Cal/g	Peak temp. °K
CROSSLINKED				
0	0.372	588.7	0.207	589.7
40	0.205	588.7	0.205	589.7
60	0.190	587.7	0.132	588.7
90	0.133	587.0	0.133	588.0
UNCROSSLINKED				
0	0.214	586.5	0.128	590.5
40	0.114	586.5	0.120	588.0
60	0.038	586.0	0.124	587.5
90	0.023	530.5	0.076	540.5

* Above data are averages of three specimens.

known, but it may be a possible hydrolysis or degradation of polymer molecular forces due to the relative humidity treatments.

The exotherm peak for crosslinked and uncrosslinked specimens produced somewhat different trends as compared to endotherm peak data. As relative humidity increases from 0 to 60%, the area under the exotherm curve for uncrosslinked specimens fluctuates slightly, and a relatively large decrease in the area under the exotherm curve is exhibited as the relative humidity increases above 60%. The exotherm peak temperature decreases slightly for uncrosslinked specimens at relative humidity levels up to 60%. Above 60% relative humidity, the exotherm peak temperature decreases sharply.

A large decrease in area under the exotherm for crosslinked specimens is evident as the relative humidity increases from 40 to 60%, while between 0–40 and 60–90% relative humidity, the exotherm peak area remains relatively constant.

The differential scanning calorimetry data for crosslinked and uncrosslinked PVAC films indicates that above 40%, particularly 60%, relative humidity, some type of degradation mechanism is occurring in the polymer structure. This trend is consistent with the tensile properties data discussed earlier.

CONCLUSIONS

Shelf-life periods from 1.5 to 3.5 months had a significant effect on the tensile strength properties but did not affect the modulus of elasticity values for both crosslinked and uncrosslinked PVAC films. Relative humidity shelf-life interaction terms were significant in the tensile strength and modulus of elasticity equations for uncrosslinked PVAC films. The contributions of shelf-life and relative humidity shelf-life interaction terms to the R^2 values of the regression equations were small compared to the contributions due to relative humidity alone. Relative humidity levels between 0 and 40% had little effect on the tensile properties, but a slight decrease in calorific values was observed for both crosslinked and uncrosslinked PVAC films. Tensile properties for both crosslinked and uncrosslinked films degraded rapidly as the relative humidity levels increased from 60 to 90%. This degrading trend was also illustrated by the rapid decrease in calorific

values as the relative humidity rose above 60%. Regression analysis established that the mechanical properties varied mainly as a function of relative humidity.

The results of this study indicate that if a composite consisting of a wood substrate and PVAC emulsion adhesive were exposed to high relative humidities, the cohesive properties of the glue line would be altered. A decrease in the mechanical properties of the glue line would occur, which could lead to glue line failure rather than the desired wood failure. This study established the need for more research on the effects of environment conditions on the properties of adhesives.

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