

ELASTOMERIC CONSTRUCTION ADHESIVES: INFLUENCE OF SOLVENT RETENTION ON STRENGTH

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(Received 15 November 1978)

ABSTRACT

Solvent retention for a styrene-butadiene elastomeric construction adhesive was determined by gas-liquid chromatography and compared to shear strength development during a 5-month cure period at ambient temperature. Both low (hexanes) and high boiling (toluene) solvents were found to be present and strength development was directly related to solvent losses.

Keywords: Adhesives, styrene-butadiene adhesive, adhesive strength, shear strength development.

INTRODUCTION

Elastomeric adhesives currently are used to join floor and wall panels to dimension lumber during construction of factory and on-the-site-built structures. The majority of these adhesives set or cure by either solvent evaporation (e.g. styrene-butadiene and polyvinyl acetate), reaction with a small amount of water (i.e. polyurethane), or by cooling (e.g. hot melts). Organic-solvent-based adhesives are often chosen for on-the-site applications because of their gap-filling properties and cure capabilities under varying climatic extremes. Increasing shear strengths with time periods of up to one year have been reported by Beech (1973) and Vicks (1971) for many wood bonds formed using solvent-based elastomeric construction adhesives. Retention of solvent in the glueline seems to be the reason for this delayed curing action.

Since it has been suggested by Hoyle (1976) that elastomeric construction adhesives in the future may be used in semi-structural applications, the rate of solvent release in solvent-based elastomeric adhesives would be of concern to the potential user. Not only could strength be affected, but also the long-term exposure of workers or building occupants to the organic solvents could pose health problems, especially if toxic solvents were used. Moreover, the presence of flammable organic solvents in the glueline also poses a potential fire hazard, especially in enclosed areas.

Several studies have been reported on solvent release from polymer films and coatings (for example: Hansen 1970; Murdock and Wiskus 1963; Newman et al. 1975; Roller and Gillham 1978; Vicks 1971; and Wilks and Gilbert 1968). Based on film and coating studies, solvent release has been observed to occur in two distinct stages. The first stage involves a rapid solvent evaporation from the film surface. The second stage involves a much slower diffusion of solvent through the polymer prior to release of solvent to the environment. This second stage predominates once the surface of the film or coating has "hardened." These solvent losses have been followed by weight loss, radioisotope tagging (Murdock and Wiskus 1963), modulus changes in films (Roller and Gillham 1978) and by

gas-liquid chromatography (GLC), (Newman et al. 1975; and Roller and Gillham 1978).

Coatings or films and adhesive gluelines will dry differently since the former usually have large surface areas exposed to the atmosphere, while the latter are mostly in contact with the substrate. In wood-adhesive bonds, solvent diffusion within and between wood and adhesive is therefore a major factor in governing bond cure.

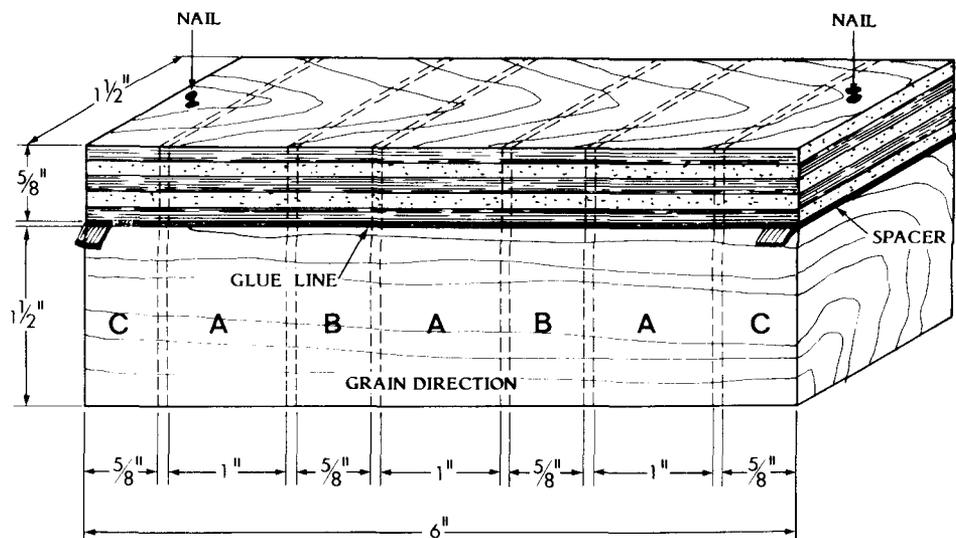
The purpose of this study was to quantify the relationship between shear strength development and elastomer solvent loss for a commercial styrene-butadiene-rubber (SBR) adhesive that was thought to contain toluene and hexane as solvents. The conditions of cure were restricted to low moisture content (MC) wood at ambient conditions and GLC was used to qualitatively and quantitatively identify the solvents present during cure.

EXPERIMENTAL

The elastomeric construction adhesive used in this study was PL-400, manufactured by B. F. Goodrich, containing about 37% solvent by weight (actual solids content was found [oven-dry method] to be 63.2%).

Two sets of samples were prepared by bonding 1½-inch × 6-inch (38-mm × 152-mm) Douglas-fir plywood strips (MC 5%) of ⅝-inch (16-mm) thickness to freshly planed Douglas-fir lumber 1⅜ inch × 1½ inch × 6 inch (35 mm × 38-mm × 152 mm) of 5% MC. Spacers 2 inch × 0.5 inch × 0.008 inch (51 mm × 12.5 mm × 0.2 mm) were placed at both ends of each sample before bonding to control glueline thickness (Fig. 1). An adhesive bead, ¼-inch diameter (6-mm), was spread lengthwise along the middle of the 1½-inch-wide lumber face. The first set comprised 15 sample blocks each fastened by two nails during cure. Glueline thicknesses ranged from 0.008 to 0.026 inch (0.2 to 0.7 mm). In an attempt to reduce glueline thickness variation, the second set (15 sample blocks) was held together under clamping pressure of 4 psi (0.03 MPa) during the first week of cure. The resulting glueline thickness ranged from 0.007 to 0.016 inch (0.2 to 0.4 mm). All sample blocks showed squeeze out along the entire glueline. Samples were stored at ambient conditions (22 C and 50% R.H.) for a period of up to 5 months.

During this 5-month period, one sample block was removed from the first set after 1, 3, 6.5, 24, 48, 72, 168, 336, 504, 672, 1,092, 1,764, and 3,024 h of cure time. Samples were removed from the clamped set after 1.5, 3.5, 16.5, 21, 27, 90, 168, 336, 672, 2,688, and 3,024 h. The remaining samples from each set were subsequently heated in a forced-air oven at 65 C for 20 h. Each sample block was cut into test specimens (25–30 g) as shown in Fig. 1. Shear tests were immediately performed (ASTM D3498-76). Specimens for solvent retention measurements were immediately placed in 24-oz (680-ml) Mason jars, and an accurately weighed amount (3 to 6 mg) of iso-octane (2, 2, 4-trimethyl pentane) was added as an internal standard. In order to prevent loss of the internal standard, it was weighed and transferred to the Mason jar while inside a capillary tube. The jar was then sealed with a Mason lid that had been modified by drilling a 7/16-inch (11-mm) hole to accommodate a ¼-inch × ⅛-inch (6-mm × 3-mm) stainless-steel (s.s.) Swagelok union fitting. A standard high-temperature silicon rubber GLC septum



- (A) SHEAR STRENGTH SAMPLES
 (B) SOLVENT RETENTION SAMPLES
 (C) END DISCARDS

FIG. 1. Cutting pattern for test specimens.

was held in place with a $\frac{1}{4}$ -inch s.s. Swagelock nut. The fitting was secured to the lid by a $\frac{1}{8}$ -inch s.s. nut clamping two $\frac{7}{16}$ -inch (11-mm) washers to which had been applied liberal amounts of silicone-rubber sealant. The lid assembly was heated at 100 C for 6 h to cure the sealant. Initially each sample jar assembly was checked for leaks by placing a known amount of iso-octane into the jars and heating them to 140 C. Gas-liquid chromatographic (GLC) analysis over a period of 3 h established whether the assembly was leakproof.

Prior to GLC analysis, each sealed jar and sample was submerged in hot water (80 C) for 1 min. If no leaks were observed, the sample jars were placed in a small air-flow oven maintained at 140 C and allowed to equilibrate for 30 min. At least three samples (0.5 to 1.0 ml) were removed for GLC analysis with a "pressure-lock" gas syringe equipped with a side port needle. The coefficients of variation observed in the GLC determinations were $\pm 3.5\%$ during the first 200 h, increasing to about $\pm 15\%$ after 1,300 h.

Gas-liquid chromatographic (GLC) analyses were performed on a Hewlett-Packard 7620A research gas chromatograph equipped with a flame ionization (F.I.) detector and a Model 3370b electronic integrator. The column temperature was maintained isothermally at 85 C, the injector port and flame detectors at 175 C. The nitrogen carrier gas was delivered at 40 ml/min. The column was 25-feet \times $\frac{1}{8}$ -inch (7,620-mm \times 3-mm) o.d. s.s. packed with 10% of SP 2100 on 80–100 mesh Supelcoport. Retention times and areas were recorded automatically. The areas were converted to weights (g) by the use of the internal standard method (Ettre and Zlatkis 1967). The internal standard (iso-octane) had a retention time of 7.0 min; the solvents peaks had relative retention times of 0.53, 0.57, 0.61, 0.71, 0.82

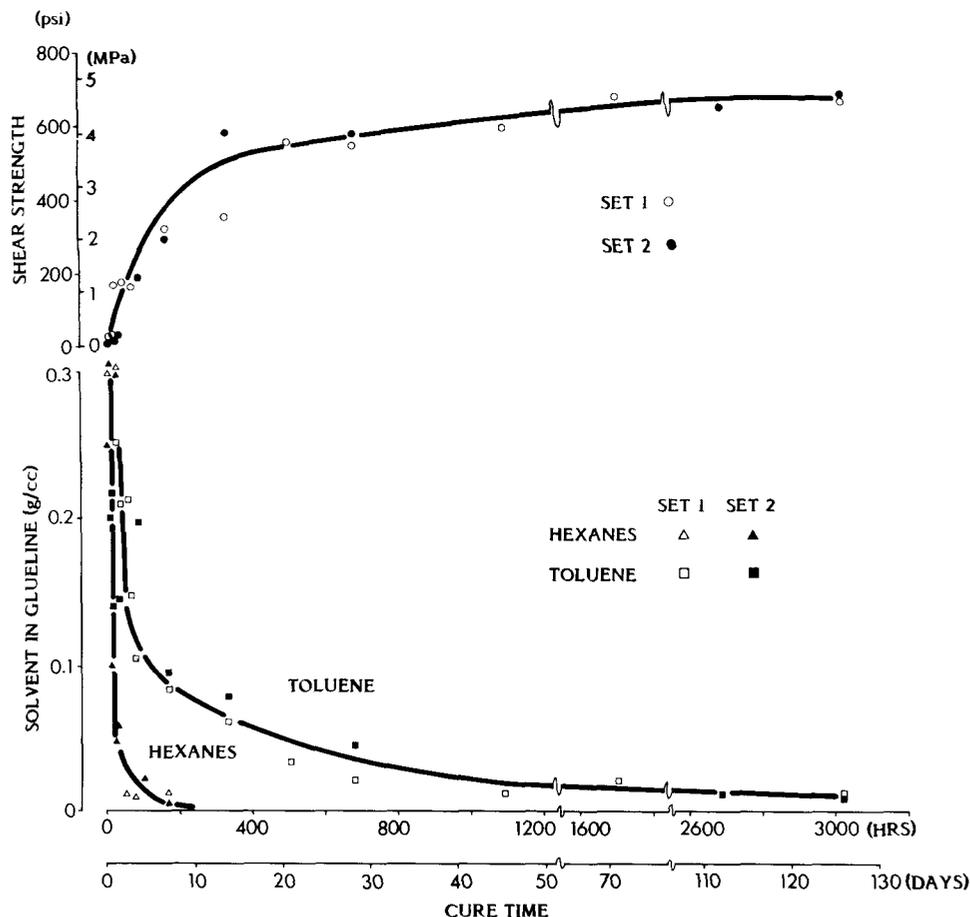


FIG. 2. Solvent loss and strength development with time for an SBR elastomeric construction adhesive.

(isomeric hexanes) and 1.51 (toluene). Solvent identities were confirmed by the usual coinjection technique (Ettre and Zlatkis 1967).

A control experiment did not produce any volatiles that could be detected by this technique. Water vapor, although visibly present is not detected by F.I. detectors.

Following GLC analysis, length and width of specimen gluelines were measured with calipers, while average gluelines thickness was determined with a microscope (50 \times magnification) using a graduated eyepiece. From these values, glueline volumes were determined.

RESULTS AND DISCUSSION

Shear strengths found during the period of cure studied are shown in Fig. 2. Strengths increased in what appears to be a two-stage process. In the first stage (up to 300 h cure) shear strength increases rapidly to about 500 psi (3.45 MPa), corresponding to about 75% of the final strength. The second stage (300 to 3,400 h) involved a very gradual increase of shear strength.

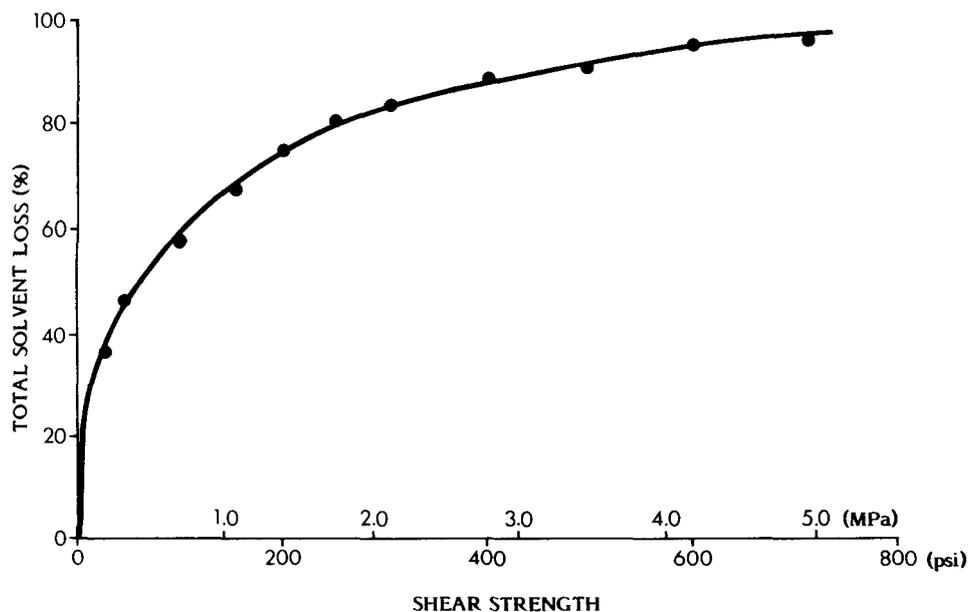


FIG. 3. Graph of percentage solvent retained versus shear strength.

The relationship between solvent retention and cure time for this elastomeric adhesive is shown in Fig. 2. Comparison of the GLC retention times with common organic solvents confirmed the high boiling (slow evaporating) solvent as toluene and identified the low boiling (fast evaporating) solvents as a mixture of isomeric hexanes. In addition, a proton magnetic resonance spectroscopic analysis of a distilled sample of the SBR construction adhesive solvent indicated only aromatic and aliphatic hydrogen functionalities. During the first 24 h of cure, about 85 and 40%, respectively, of the hexanes and toluene solvents were lost. After 200 h, almost all the hexanes and about 65% of the toluene had left the glueline. Even after 3 months of cure, 10% of the toluene was still present in the glued specimen. Both nailed and pressed sample blocks showed similar solvent loss tendencies, although glueline thickness ranges were different.

The occurrence of two stages of cure observed here could easily be altered by fluctuations in ambient temperature and wood moisture content. There is no question that the rate of solvent loss will be enhanced at elevated temperature, with subsequent quicker build up in strength if "cure" occurs at temperatures above those experienced in this study. However, as shown by this study, not all the solvent leaves the glueline, even if the glued specimen is heated to 65 C for 20 h. Some toluene appears to be trapped in the adhesive matrix where it may act as a plasticizer.

The direct relationship between total solvent loss and shear strength development is more clearly illustrated in Fig. 3. During the initial stages of cure, the total solvent losses are rapid, 75% being lost before the shear strengths reach 200 psi (1.32 MPa). The bulk of the solvent lost during this stage was the hexanes (95% having left the glueline). The major strength buildup occurs, however, during the last 25% of total solvent loss where the higher boiling toluene is removed

at a much slower rate. Here, loss of further solvent is retarded by the thickening of the polymer matrix which likely makes solvent diffusion rather than solvent evaporation the dominant mechanism. The overall curvilinear relationship between solvent loss and shear strength demonstrates the direct role of solvent in strength development for this SBR adhesive.

Examination of a "cured" (ambient temperature) specimen of this SBR adhesive revealed that it could be easily solubilized in the identified solvent mixture. This solubilization confirmed that, at least for SBR adhesives, "cure" results from solvent loss and not from crosslinking reactions occurring prior to, or following, solvent release from the adhesive matrix.

Solvents present in mastic construction adhesives, such as SBR, provide for flow during assembly. Too rapid-evaporating solvents allow insufficient assembly and flow times, while slow-evaporating solvents allow too much plastic flow to occur before the necessary bonding strength is developed to support the weight of the bonding components. The choice of solvents is thus a compromise between these factors and the cost of solvents.

CONCLUSIONS

Continual solvent release from the SBR adhesive glueline is the reason for its long-term shear strength development. Although this study was limited to one adhesive system cured under ambient conditions, these general stages of "cure" development should be present in other solvent-based elastomeric systems. This "cure" property must be considered when the glueline in question may come under mechanical stress during fabrication or in service. Temperature, humidity, moisture content of the wood and wood species are also factors that could alter the "cure" rate of these types of gluelines. Also similar base polymer systems may perform differently during "cure" because of differences in solvents, solvent ratio, or molecular weight distribution in the polymer, which could favor the evaporation mechanism or enhance the diffusion rate.

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