ORIGINAL ARTICLE

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Effect of the ethylene/vinyl acetate ratio of ethylene–vinyl acetate emulsion on the curing behavior of an emulsion polymer isocyanate adhesive for wood

Abstract We investigated the curing behavior of an emulsion polymer isocyanate adhesive for wood with different ethylene–vinyl acetate (EVA) emulsions, because it was found that the ethylene/vinyl acetate weight composition (E/VA ratio) of EVA could control the volume of gas emitted from the adhesive. EVA with higher VA content reduced the volume of gas emitted at the initial stage, which was caused by the extent of the reaction between the NCO groups and water. The reaction scheme of NCO could not be determined because the broad infrared (IR) absorptions due to $CaCO_3$ and water masked the information of the NCO products in IR spectra. Examination of the degree of swelling suggested that the adhesive films stored for 3 weeks had the same degree of cross-linking structure in spite of the variation of EVA. This result was supported by IR spectroscopy, which showed the same amounts of NCO remained in these films. All the adhesives prepared in this study had satisfactory bond performance. The findings indicate that the E/VA ratio affects the curing behavior of the adhesive in the initial curing stage, whereas the cross-linking structure and the bond performance were independent of the E/VA ratio after storage for 3 weeks.

Key words Isocyanate · Ethylene–vinyl acetate copolymer · API · EPI · Wood adhesive

Introduction

Japanese Industrial Standard (JIS) K 6806 defined an emulsion polymer isocyanate (EPI) adhesive as "water based polymer–isocyanate adhesive for wood." This adhesive was developed in the early 1970s and was originally named "aqueous vinyl polymer solution–isocyanate adhesive." Its abbreviation, API, has become its popular name rather than the JIS defined name. API is a two-component adhesive system: a water-based glue comes with an isocyanate (NCO) cross-linker. Typically, the water-based glue is a mixture of poly(vinyl alcohol) (PVOH) solution, emulsions such as poly(styrene-co-butadiene) (SBR) and poly(ethylene-co-vinyl acetate) (EVA), calcium carbonate ($CaCO_3$) as filler, and a small number of additives. The cross-linker is commonly a crude form of polymeric methylene bis-(phenyl isocyanate) (pMDI).

Several groups have published both the mechanical and chemical properties of API. Taki et al. have studied API extensively to determine its mechanical and chemical characteristics,[1–8] such as the relationship between the cross-linking density and the adhesive strength, the influence of stored condition upon its mechanical properties, the reaction mechanism of the model API adhesive, and its adhesive properties over a wide temperature range. Recently, Yamada et al.[9] used acetoacetylated poly(vinyl acetate) (PVA) to improve the adhesive performance of API. Umemura et al. have widely studied the durability of isocyanate resin adhesive under various stored conditions.[10–12]

While many studies have been carried out to elucidate the character of API, we think that its chemical nature in particular has not been fully clarified. For example, it is known that EVA is more effective than SBR in improving the initial bond strength of API adhesive,[13] although the addition of EVA occasionally causes undesirable foaming after mixing (see Fig. 1). In industrial use, this foaming could lead to a defective glue line, by which the bond performance would decrease. Foaming is considered to result from the release of carbon dioxide (CO_2) where NCO groups react with water to produce primary amine groups via carbamic acid.[6]

We commenced this study to reduce the gas emitted from API adhesive with EVA emulsion. We examined factors such as the viscosity and pH of the base glue, the

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amount of surface-active agent and the ethylene/vinyl acetate weight composition ratio (E/VA) ratio of EVA, and the particle diameter of $CaCO_3$. The results showed that all of the examined factors affected the volume of the emitted gas. It was found that the gas decreased significantly by varying the E/VA ratio of EVA emulsion when compared with an API with a commercial EVA. In this study, to elucidate the effect of the E/VA ratio of EVA on the curing behavior of API, we examined the volume of emitted gas, the degree of swelling, dynamic viscoelastic behavior, and wood bonding performance, together with infrared (IR) spectroscopic data.

Experimental

Materials

Three EVAs, designated as EVA-vaH, EVA-vaM, and EVA-vaL, were employed for this study; they differed in the E/VA ratio where the order of the contained VA was EVA-vaH > EVA-vaM > EVA-vaL. The E/VA ratio was controlled by the initial ratio of ethylene and vinyl acetate monomers in the synthesizing reactor, which was estimated with the infrared absorbance of C=O stretching (at 2930 cm^{-1}) compared with that of CH_2 stretching (at 1730 cm^{-1}). The other properties of the EVA samples, such as solid content, viscosity, pH, and kinds and amounts of emulsifiers, were similar. These characteristics are summarized in Table 1. The three EVA samples were specially synthesized by Denki Kagaku Kogyo (Tokyo, Japan).
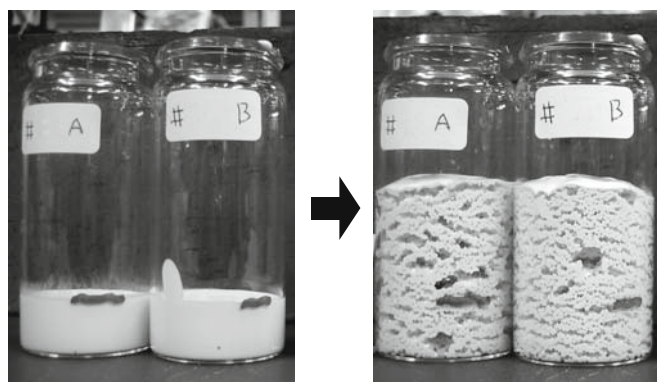
Fig. 1. An example of undesirable foaming in an emulsion polymer isocyanate adhesive. *Left*, just after mixing; *right*, after standing for 60 min

PVOH was purchased from Sigma-Aldrich and was 99%+ hydrolyzed with a molecular weight range of 89 000 to 98 000. It was dried under reduced pressure at 60°C for 1 day, and thereafter was dissolved in hot water by adding gradually with stirring to give a 15% (w/w) solution. The solution was kept at 60°C with stirring for 6 h and was subsequently stirred at room temperature for 1 day.

pMDI (Milionate MR-200; Nippon Polyurethane Industry, Tokyo, Japan) was used as received. It was mainly composed of 4,4′-MDI oligomers, contained no solvent such as toluene or xylene, had a viscosity of 163 mPa·s (25°C), NCO molar concentration of 7.27 mmol/g (NCO content of 31.0%, w/w), and specific gravity of 1.23 at 25°C.

Calcium carbonate was a commercial product for API use, with a median particle diameter of 1.36 μm. It was used as received. Water was purified with a Millipore Elix 5 water purifier to give a specific electrical conductivity lower than 0.5 μS/cm. Other chemicals were purchased from Wako (Tokyo, Japan) and used as received.

Preparation of adhesive

Three of the base glues were prepared with 45 parts of the EVA emulsion (EVA-vaH, EVA-vaM, or EVA-vaL), 25 parts of PVOH solution, and 30 parts of $CaCO_3$. They were blended with a blade agitator at 700 rpm for 3 h.

The API adhesives were prepared with the base glues and the cross-linker in the weight ratio of 100/15. They were mixed together for 3 min and degassed for 30 s with a homogenizer (HM-500 hybrid mixer, Keyence, Osaka, Japan). This mixture was cast onto Teflon sheets (15 × 15 cm) and spread with a glass rod to form a film sample of ca. 1 mm thickness.

The samples on Teflon sheets were separated into two groups; one group was immediately packed in a sealed desiccator to measure the volume of gas emitted (detail is described in subsequent section), the other was examined for infrared spectroscopy, the degree of swelling, and dynamic mechanical analysis. Both groups were stored at 23°C at 50% relative humidity (RH). After storage for 2 weeks, the specific density was approximately 0.9 for all films.

Volume of emitted gas

Figure 2 illustrates the measuring apparatus designed for this experiment.[6] Each measurement used 100 g of the

Table 1. Characterization of ethylene–vinyl acetate (EVA) emulsions

EVA type	Vinyl acetate ratio (%, w/w)	Solid content (%, w/w)	Median particle diameter^a (μm)	Viscosity^b (mPa·s)				pH
				6 rpm	12 rpm	30 rpm	60 rpm	
EVA-vaH	86.6	54.6	0.53	10 600	7 250	4 500	3 300	4.9
EVA-vaM	82.4	55.0	0.60	9 000	6 250	3 880	2 830	4.9
EVA-vaL	78.7	55.1	0.78	8 900	6 000	3 800	2 900	4.7

^{a} Calibrated by zeta potential with a zetasizer
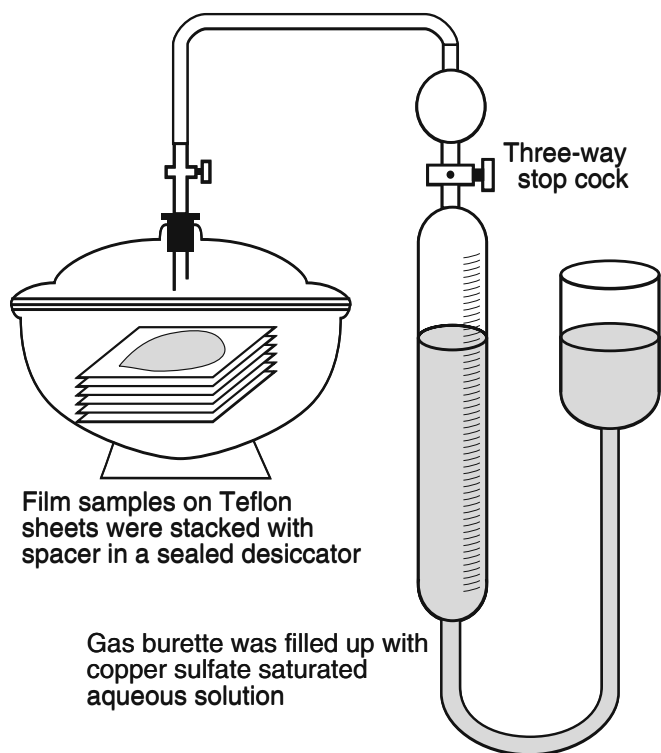^{b} Measured with a rotary viscometer type BM using rotor No. 4 at 30°C

Fig. 2. Measuring apparatus for the emitted gas

Fig. 3. Cross-lap testing specimen for wood bonding performance

adhesive sample, where ten Teflon sheets with sample (10 g per sheet) were stacked with spacers in a sealed desiccator (internal volume ca 8 l). The desiccator was connected to a 500-ml gas burette. The burette was filled with saturated copper sulfate aqueous solution to stop the emitted gas from dissolving. The volume of the gas emitted from the sample was measured as the volume of gas collected in the burette. The collected gas was purged from the burette via a three-way tap after each measurement.

Infrared spectroscopy

Infrared spectra were recorded for the samples stored for 1, 7, 14, and 21 days. These samples were collected after the designated period, powdered by a cutter mill while cooled with liquid nitrogen, mixed with KBr, and compressed into IR disks. IR spectra were recorded on a Nicolet Magna-IR 860 Fourier transform spectrometer with a DTGS detector with the analytical chamber conditioned with a continuous flow of dry air at 23°C. The number of scans was 256 and spectral resolution was 4 cm^{-1}.

Degree of swelling

The samples stored for 1 day and 2 weeks were cut into pieces measuring 2×2 cm and then weighed. They were immersed into well-dehydrated dimethyl sulfoxide with di-n-butylamine that inhibited further isocyanate reaction. After being immersed for 2 weeks at room temperature (ca. 23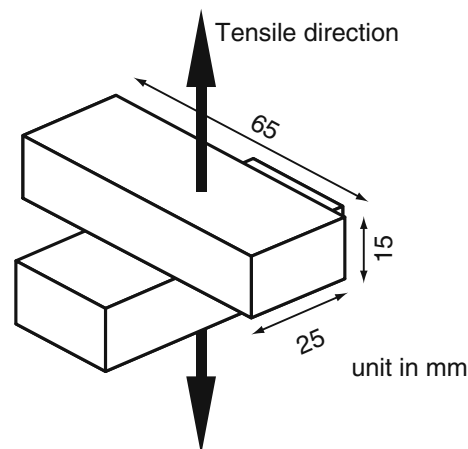°C), the swollen samples were delicately wiped to remove the immersing medium, and subsequently weighed again to estimate the degree of swelling (DS). DS was calculated by the following equation:

DS (wt%) = $W'/W \times 100$

where W' and W denote the weight of the swollen and untreated sample, respectively. Experiments were carried out in triplicate for each sample, and DS was reported as the average value.

Dynamic viscoelastic behavior

Dynamic viscoelastic behavior of the sample was measured with a dynamic mechanical analyzer (DVA-200s, ITK, Osaka, Japan), with a heating rate of 2°C/min in the temperature range between −100° and 300°C. Measurements were conducted in the tensile mode at a frequency of 5 Hz with continuous flow of dry N_2 gas through the measuring chamber.

Wood bonding performance

Wood bonding performance of the adhesive was evaluated by the tensile bond strength at breakage and the percentage of wood failure. The wood adherent block was birch (*Betula maximowicziana* R., 65 mm long × 25 mm wide × 15 mm thick), with the radial face acting as the adhesive face. The blocks were conditioned at 23°C and 50% RH until their moisture content became constant (ca. 11%, w/w).

The adhesive was applied to one side of the two blocks with a coverage of approximately 200 g/m^2. The blocks were bonded together in a crossing orientation (so-called cross-lap, illustrated in Fig. 3), where the adhesive area was 25 × 25 mm. The bonded blocks were pressed at 10 kg/cm^2 for 1 day, and thereafter were stored at 23°C and 50% RH for 2 weeks.

The tensile bond strength at 23°C was recorded by a tensile tester (Tensilon UCT-5T, A and D, Tokyo, Japan), with the tensile direction vertical to the bondline at a

crosshead speed of 10 mm/min. Seven specimens were tested for each of the API adhesives. The data for the tensile strength at breakage and the percentage of wood failure were reported in accordance with JIS K 6848 ("Adhesives—testing methods of bonding strength of adhesives").
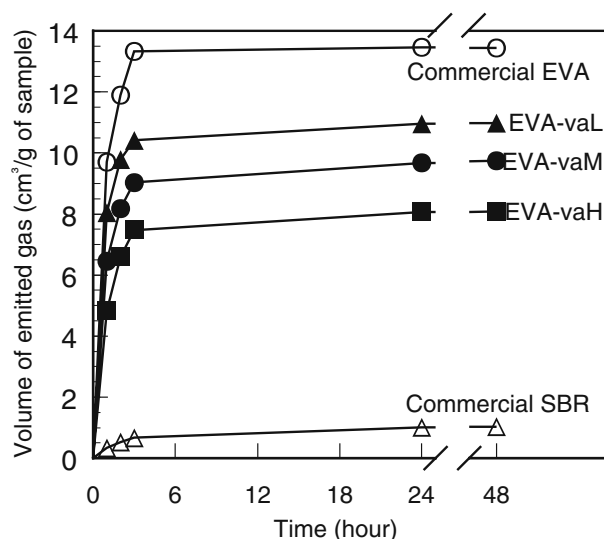
Results and discussion

Volume of emitted gas

Figure 4 shows the time dependency of the volume of gas emitted from the film samples. For some samples the volumes were measured for 2 weeks, but their volume of emitted gas showed little change compared with those measured for up to 48 h. All the samples emitted most of the gas within 3 h, and after 24 h the gas emission had almost stopped. The emitted gas is CO_2 derived from the reaction between NCO groups and water, which occurs vigorously within 3 h and is near completion after 24 h.

The volume of emitted gas decreased with increasing VA concentration in EVA; its order was EVA-vaL > EVA-vaM > EVA-vaH. We consider two explanations for the result: (1) EVA with higher VA concentration reduces the reaction of NCO with water, and (2) the gas might remain in the film due to an effect of EVA with high VA. These two explanations were later validated by FT-IR measurement focused on NCO reactions.

Figure 4 also shows reference data obtained from samples prepared with commercial EVA and SBR. The film prepared with a commercial EVA released approximately 13 times as much gas as that with a commercial SBR in 48 h (13.4 and 1.0 cm^3/g, respectively). Supposing that all NCO groups react with water to produce primary amine groups, 14.2 cm^3/g of CO_2 is released stoichiometrically from each of the samples. This result demonstrates that undesirable foaming occurs in the case of the adhesive with EVA, but not with SBR.
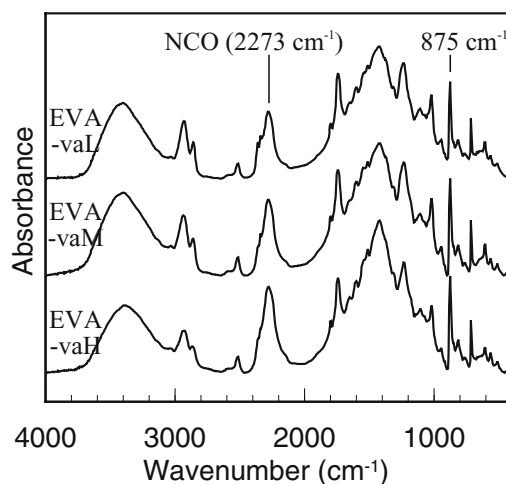
Infrared spectroscopy

Figure 5 shows the IR spectra of the adhesive samples stored for 1 day at 23°C and 50% RH. The spectra were normalized at 875 cm^{-1} for the sharp peak due to $CaCO_3$.
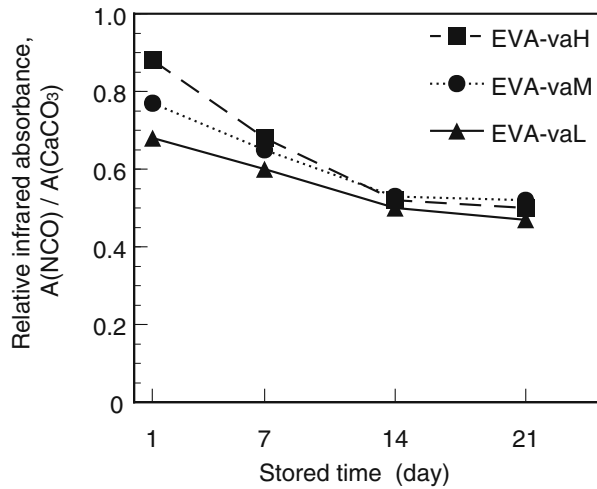
The peak at 2273 cm^{-1} is assignable to NCO asymmetric stretching; its intensity became strong with high VA concentration in EVA. We evaluated the relative absorption ratio of the peaks, A (2273 cm^{-1})/A (875 cm^{-1}); this ratio could be interpreted as the amount of residual NCO groups. The ratio of the sample with EVA-vaH was 0.88; correspondingly, that of EVA-vaM was 0.77 and that of EVA-vaL was 0.68. Thus, the order of the ratio was EVA-vaH > EVA-vaM > EVA-vaL, which is the reverse of the trend for the volume of emitted gas as discussed above. This result confirms that EVA with higher VA concentration reduces the reactivity of NCO with water during the initial stage. We have no clear reason that can explain this phenomenon. Some morphological observations are needed to clarify the phenomenon, and we are yet to execute this phase of the investigation.

On the other hand, the reaction of the NCO group in the adhesive could not be verified based on the IR spectra. The reaction products from NCO have two strong absorbances in the infrared region, which are C=O stretching in the range 1640–1740 cm^{-1} and N—H stretching around 3300 cm^{-1}. These characteristic bands were not distinguished because the C=O stretching region was covered with the huge band due to $CaCO_3$ centered at 1400 cm^{-1}, and the N—H stretching bands overlapped with the broad band assignable to water.
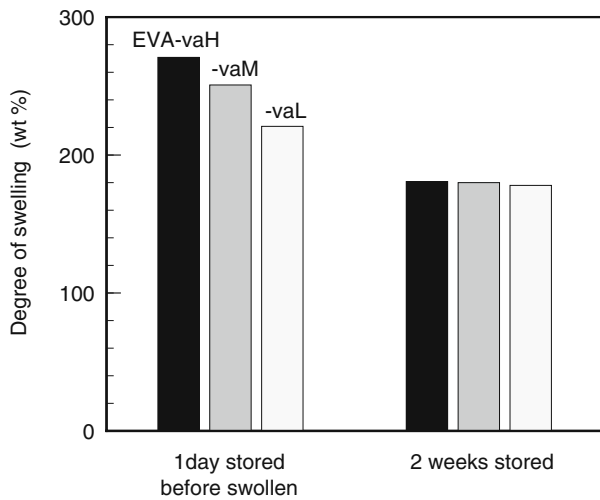
Figure 6 shows the dependence on storage time for the relative absorption ratio of NCO normalized by the same

Fig. 4. Time dependence of the volume of total gas emitted from the films. *EVA*, poly(ethylene-*co*-vinyl acetate); *EVA-vaL*, EVA with low vinyl acetate content; *EVA-vaM*, EVA with medium vinyl acetate content; *EVA-vaH*, EVA with high vinyl acetate content; *SBR*, poly(styrene-*co*-butadiene)

Fig. 5. Infrared spectra of the samples. The spectra were normalized by the sharp peak at 875 cm^{-1}

Fig. 6. Dependence of relative absorption ratio of NCO on storage time

Fig. 8. Storage modulus E' (*upper dataset*) and loss modulus E'' (*lower dataset* and *inset*) of the film samples. *Squares*, EVA-vaH; *circles*, EVA-vaM; *triangles*, EVA-vaL
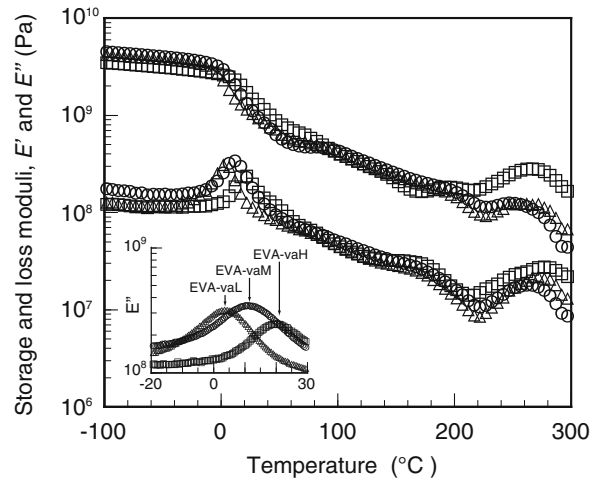

Fig. 7. Degree of swelling of the film samples

manner described above. The relative absorption ratios of NCO differed at the initial stage, whereas the difference became small with storage time. After 14 days the ratios did not change and were about the same value. This result implies two points: (1) the residual NCO groups react gradually up to 14 days, and (2) after a proper storage period there is little difference in the residual NCO amounts between the samples in spite of the variation of EVA.

Degree of swelling

We confirmed cross-linking structures of the samples because the structure should be affected by NCO reactions developing in the system. The degree of cross-linking structure can be estimated by DS,[14] where higher DS means higher cross-linking structure. Figure 7 shows the DS for the samples with different EVA and storage times of 1 day or 2 weeks before swelling.

For the samples stored for 1 day, DS increased with increasing VA concentration in EVA. This means that the formation of the cross-linking structure was promoted by the high VA concentration in EVA at the initial curing stage. On the other hand, it was the same for the samples stored for 2 weeks. This implies that the cross-linking density of the samples stored for 2 weeks is independent of the EVA type used. This tendency agrees with the result of the IR spectroscopy.

Dynamic viscoelastic behavior

Figure 8 shows the storage modulus (E') and loss modulus (E'') of the film samples stored for 2 weeks. Two differences were observed among the plots. First, the EVA types used in this study have glass transition temperatures in the range of 0°–20°C (shown in the inset of Fig. 8), with the difference attributed to the composition ratio of ethylene versus vinyl acetate. Second, the E' of the sample containing EVA-vaH was higher than those of the others above 200°C. According to rubber elastic theory,[15] this result means that the sample with EVA-vaH had higher cross-linking density than those with other EVA types. This interpretation, however, disagrees with the results for DS, where the variation of EVA had no effect on the cross-linking density of the sample stored for 2 weeks. A possible explanation for the disagreement is that E' might be elevated by the cross-linking structure newly produced by the reaction of residual NCO groups during the dynamic mechanical measurement.

Wood bonding performance

Figure 9 shows tensile bond strength and wood failure of the cross-lapped wood specimens. All the tested adhesives showed satisfactory bond performance at 23°C; the average of the tensile bond strength exceeded 45 kg/cm^2 (4.4 MPa),
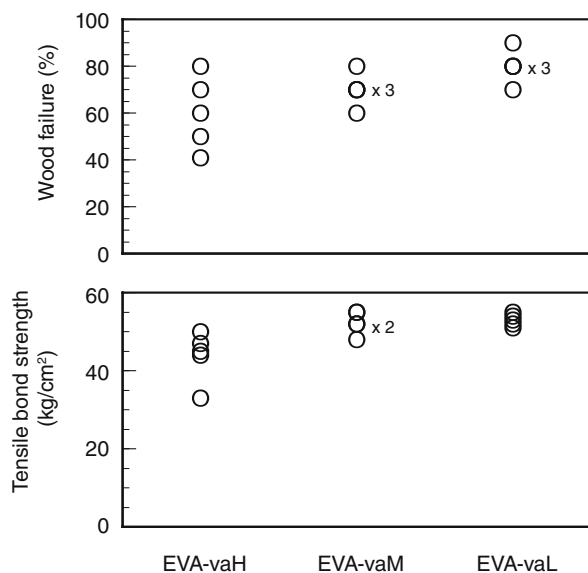
Fig. 9. Tensile bond strength and wood failure of cross-lapped specimens

and the average wood failure was over 60% for each of the adhesives. The results demonstrated that the gas emission had no effect on the bond performance of the adhesive system.

JIS K 6806 claims that an API adhesive for structural use must provide 9.81 MPa (100 kg/cm^2) of compression shear bond strength at room temperature. Our testing method is different from the JIS testing method; generally, the bond strengths obtained from the different methods could not be compared. We note that the bond strengths measured by the tensile testing with cross-lapped blocks were weaker than those measured by both the compression and tensile shear tests.

The adhesive with EVA-vaH had larger variances in both the bond strength and wood failure than the others. These variances result from the viscoelastic behavior of the adhesive at the testing temperatures; the adhesive with EVA-vaH had a peak of E'' near the tested temperature as shown in Figure 8. Thus, a slight difference in the temperature would lead to changes in its viscoelasticity, which affects the bond performance.

Conclusions

We investigated the curing behavior of an emulsion polymer isocyanate adhesive for wood with ethylene–vinyl acetate emulsions (EVA) that differed in the ethylene/vinyl acetate weight composition (E/VA ratio). The higher VA content of EVA resulted in less gas being emitted from the adhesive at the initial stage, due to decreased reaction between isocyanate and water. Both the cross-linking structure and the bond performance of the adhesives stored for 2 weeks were independent of the EVA type used. These results were supported by the analysis of IR spectroscopy where the samples stored for 2 weeks consumed the same amount of NCO groups. The findings on the relationship between the E/VA ratio and the NCO reaction are summarized as follows: the E/VA ratio affects the NCO reaction at the initial curing stage, whereas after a proper storage period the differences in both the cross-linking structure and the bond performance of the adhesive are small in spite of the variation of EVA. We could not find a solid reason for why the E/VA ratio affects the isocyanate reaction. This question requires further detailed study that should include morphological and/or microscopic examination.

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