Curing of Silylated Polyurethane with BF$_3$-Monoethylamine Complex as Moisture-Curable Adhesives and Their Properties

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ABSTRACT: Boron trifluoride monoethylamine complex (BF$_3$-MEA) was evaluated as one of the curing catalyst, for the moisture-curable adhesive based on the polyurethane end-capped with trimethoxysilane (silylated polyurethane). BF$_3$-MEA worked as the catalyst of condensation reaction of trimethoxysilyl groups in silylated polyurethane to give the corresponding networked polymer. The curing speed, the bond strength, and the heat resistance of the cross-linked adhesives with BF$_3$-MEA were compared with dibutyltin dimethoxide. It was found that BF$_3$-MEA was a good curing catalyst, which showed the same performance in the bond strength and remarkable advantages in the curing speed and the heat resistance, compared with organotin compound. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3165–3170, 2007

Key words: adhesives; catalysts; networks; polyurethanes; silicones

INTRODUCTION

Recently, much attention has been paid to water-based and solvent-free adhesives and coatings from an environmental perspective.[1–6] In particular, curing shrinkage, which is a representative inadequacy in typical solvent-based adhesives, hardly occurs and so-called VOC (volatile organic compound) can be avoided using the solvent-free adhesives in this system.[7–9] One-component type adhesives are now appreciated in the market, due to their easy handling ability and their balanced performance, in which mixing is not necessary before the application. Elastic adhesives have been used for the adhesion of various materials having different expansion coefficients, because of their excellent properties, such as good adherence, good subserviency to the substrates, and good vibration suppression.[10–12]

Recently, we developed various polyurethanes end-capped with trialkoxysilanes (silylated polyurethanes),[13–16] which can be used as a base-polymer for one-component elastic adhesives in solvent-free system. The silylated polyurethanes are known as moisture-curing polymers, which can undergo the curing by condensation reaction in the presence of water giving off alcohol compounds.[17–22] In a previous study,[16] we demonstrated the synthesis of silylated polyurethanes with commercial primary aminosilane (3-aminopropyltrimethoxysilane) and their application as a base polymer for the moisture-curable adhesives (Fig. 1). One of the crucial points of this system is a curing reaction of the alkoxysilane-terminated polymer. The curing mechanism is shown in Scheme 1, which is accelerated by catalysts (e.g., organometallic compounds, like organotin and organotitanium compounds).[23,24] In general, several catalysts are used for the preparation of one-component adhesives or coating using the alkoxysilane-terminated polymers as a base polymer, because the fast curing speed is required in these fields. Unfortunately, most of the useful organometallic compounds are hazardous to human health and environment. Another drawback is the fact that a large quantity of organometallic compounds (e.g. 1–5 wt % for the base polymers) is required to cure quickly within a reasonable reaction time. Additionally, organometallic compounds have a risk to decompose the components of adhesives, such as the compounds with ester group or urethane group and even possibly the adherends, like polyester or polyurethane. Hence, it is eagerly desired to develop novel environmentally friendly catalysts with higher efficiency and less amounts of metal content.

In this study, we focused on BF$_3$ complexes, which are well-known as one of the most conventional
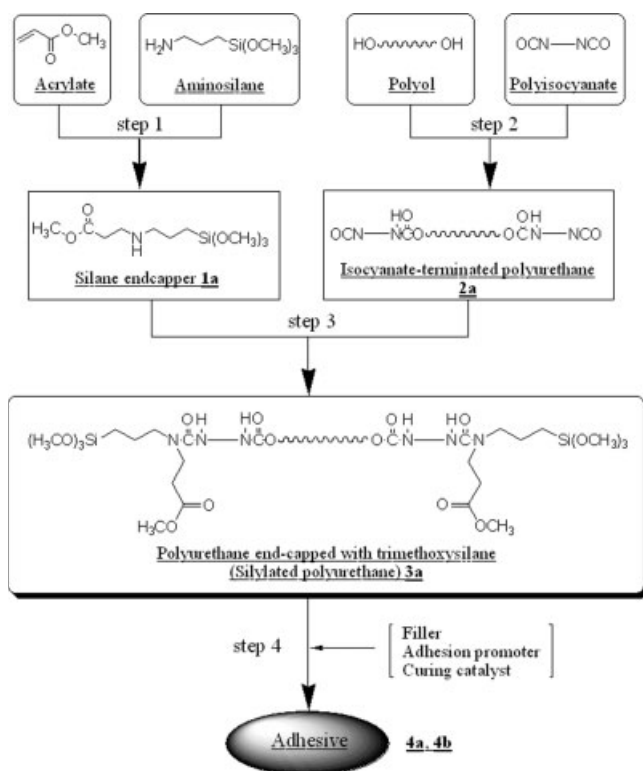
Figure 1 Pathway to prepare silylated polyurethane-based adhesives.

strong Lewis acids. For example, BF₃-diethyl ether complex has been used as the catalyst for cationic polymerization,[25,26] and BF₃-amine complexes [e.g., BF₃-monoethylamine complex (BF₃-MEA), BF₃-piperidine complex] have been used as the curing catalyst for epoxy resin.[27–29] Although the effect of BF₃-MEA catalyst for condensation reaction of alkoxysilyl groups was described,[30] the BF₃ complexes have not been used as the curing catalyst of the adhesives based on alkoxysilane-terminated polymer. In this contribution, we evaluated the effectiveness of BF₃-MEA as the curing catalyst of adhesives based on silylated polyurethanes, in terms of the curing speed, the adherence, and the heat resistance.

EXPERIMENTAL

Materials

The following reagents and materials were used without further purification: polypropylene oxide (PPO, hydroxyl value* = 11.7, M_n = 10,000, PML S 4012, Asahi Glass Urethane, Kamisu, Japan), isophorone diisocyanate (IPDI, Sumika Bayer Urethane, Amagasaki,

*Hydroxyl value is defined as the number of milligrams of potassium hydroxide required to neutralize the acetic acid capable of combining by acetylation with 1.0 g of sample.

Japan), methyl acrylate (MA, Toagosei, Tokyo, Japan), 3-aminopropyltrimethoxysilane (Shin-Etsu Chemical, Tokyo, Japan), dioctyltin diversatate (DOTDV, Nitto Kasei, Osaka, Japan), dibutyltin dimethoxide (DBTDM, Sankyo Organic Chemicals, Kawasaki, Japan), BF₃-monoethylamine complex (BF₃-MEA, Wako Pure Chemical Industries, Osaka, Japan), and clay filler [Optiwhite, Burgess Pigment Company (Sandersville, GA), the diameter measured by Micronscan analyzer (Quantachrome): 1.2 μm].

Preparation of silylated polyurethane

Silylated polyurethane 3a

The synthesis of silylated polyurethane **3a** was conducted by the reaction of silane endcapper **1a** and isocyanate-terminated polyurethane **2a** (Fig. 1), according to a method reported previously.[16] The synthesis of silane endcapper **1a** was conducted by the reaction of 3-aminopropyltrimethoxysilane and methyl acrylate. The synthesis of isocyanate-terminated polyurethane **2a** was conducted by the reaction of PPO and IPDI with DOTDV as a catalyst. ¹H NMR (CDCl₃, δ in ppm): 1.10–1.29 (br, CH₂CH (*CH₃*)), 3.24–3.80 (br, *CH₂CH*(CH₃). ¹³C NMR (CDCl₃, δ in ppm): 17.4 (br s, CH₂CH(*CH₃*)), 17.5 (br s, CH₂CH(*CH₃*)), 18.1 (br s), 18.3 (br s), 18.5 (br s), 73.0 (br, CH₂*CH*(CH₃)), 73.4 (br s, CH₂*CH*(CH₃)), 75.1 (br s, *CH₂*CH(CH₃)), 75.3 (br s, *CH₂*CH(CH₃)), 75.5 (br, *CH₂*CH(CH₃)), 155.2 (NHC(=O)O), 157.8 (NHC (=O)N), 172.6 (*C*(=O)OCH₃), 172.9 (*C*(=O)OCH₃). IR (NaCl plate): 668, 824, 868, 927, 1014, 1109, 1253, 1297, 1344, 1373, 1456, 1527, 1655, 1720, 2869, 2931, 2971, and 3359 cm⁻¹.

Preparation of silylated polyurethane-based adhesives 4a and 4b

The silylated polyurethane **3a** (500 g) and clay filler (Optiwhite, 50 g) were mixed and dried at 100°C for 1 h *in vacuo*. After cooling to room temperature, adhesion promoter (3-aminopropyltrimethoxysilane, 45 g) and curing catalyst (BF₃-MEA, 0.50 g, 0.89 mmol) were added under nitrogen and mixed at room temperature for additional 10 min under reduced pressure. Then, the mixture was subdivided into hermetically-closed cartridges, and aged at 50°C for

R = methyl, ethyl, propyl, butyl, etc
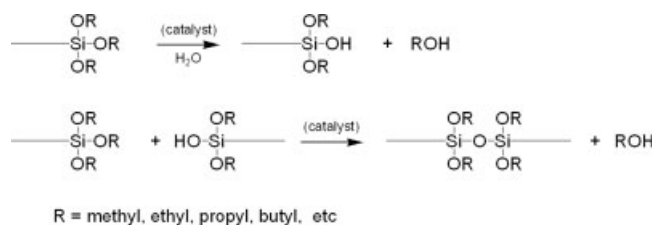
Scheme 1 Curing mechanism of alkoxysilyl-terminated polymer.
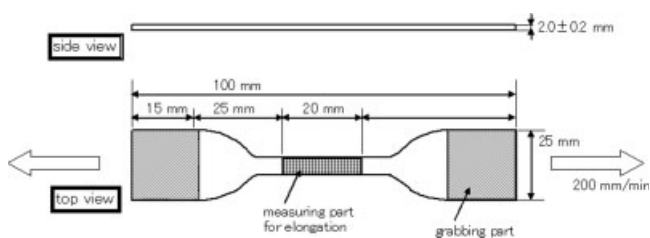
Figure 2 Illustration of dumbbell no. 3 specimen of JIS K 6251 for physical properties measurements.

Figure 3 Illustration of specimen for tensile shear bond strength measurement.

3 days to afford **4a** as a white viscous paste. The viscosity of **4a** was 50,000 mPa s. In the same manner, 1.31 g (0.89 mmol) of DBTDM was used instead of BF$_3$-MEA to afford **4b** as a white viscous paste. The viscosity of **4b** was 40,000 mPa s. The curing speeds, the tensile shear bond strength, and the heat resistance of **4a** and **4b** were evaluated.

Characterization and evaluation

FTIR spectra were recorded with a Nicolet AVATAR 360 FT-IR spectrometer system. ^{1}H NMR and ^{13}C NMR (400 MHz) spectra were measured on a JEOL ECX-400 spectrometer using tetramethylsilane as an internal standard. The viscosity was measured with a B-type viscometer (No. 7 rotor, 10 rpm, Model BH) at 23°C. The curing speed of the adhesives was evaluated as the film formation time at 23°C under 50% relative humidity. The film formation time is the period from the time the adhesives are exposed at 23°C under 50% relative humidity to the time the cured film generates on the surface of the exposed adhesives. The physical properties, including the tensile strength at break, elongation at break, 100% modulus, and 50% modulus, were measured using dumbbell no. 3 of JIS K 6251 (Fig. 2) with an AUTO-GRAPH AGS-100B (Shimadzu Corporation) at tensile speed of 200 mm/min. Tensile shear bond strength was measured with AUTOGRAPH AG-50kNE (Shimadzu Corporation) at a tensile speed of 5.0 mm/min. During this test, shear stress was applied across the adhesive bond, and the bonded materials were forced to slide over each other with the adhesive bond layer providing the resistive force (Fig. 3). The substrates (25 × 100 mm^2) for the tensile shear bond strength measurement were Al (aluminum, thickness = 2.0 mm), PMMA (polymethylmethacrylate, thickness = 3.0 mm), and ABS (thickness = 3.0 mm), respectively. Each substrate was adhered with the adhesive **4a** or **4b** and the bonded test piece was cured at 23°C under 50% relative humidity for 1 day and then at 50°C under 95% relative humidity for 1 day. Each substrate for the heat resistance test was adhered with the adhesive **4a** or **4b** and the bonded test piece was cured at 23°C under
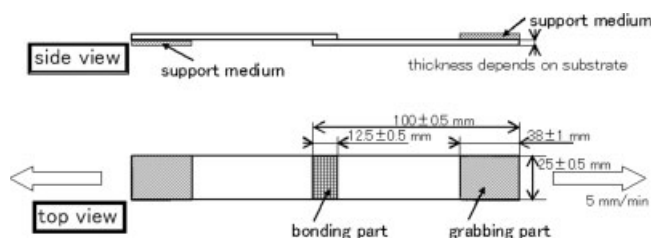
50% relative humidity for 1 day and then at 50°C under 95% relative humidity for 1 day (initial in Fig. 10). After curing, part of the test pieces was exposed at 80°C or 105°C for 1 week (Fig. 10). After curing and exposure, the tensile shear bond strength was measured, pursuant to JIS K 6850.

RESULTS AND DISCUSSION

Comparison of curing speed between BF$_3$-MEA and DBTDM

The curing speed was compared by the film formation time, in which 0.1–5.0 mmol of BF$_3$-MEA or DBTDM was added to 100 g of **3a**, respectively. Figure 4 shows the film formation time of **3a** with 0.1–5.0 mmol of BF$_3$-MEA or DBTDM, and Figure 5 is the magnification of the area from 1.0 to 5.0 mmol. Under the same molar content of the catalyst, BF$_3$-MEA cured **3a** much faster than DBTDM. Further, the film formation time was within several seconds, when the amount of added BF$_3$-MEA was more than 3.0 mmol. It means that BF$_3$-MEA could promote the curing speed ultimately. In other words, BF$_3$-MEA has the ability to cure the silylated polyurethane instantaneously under ambient humidity. On the contrary, DBTDM could be acted only as a limited role, because the film formation time with 5.0 mmol of DBTDM was almost the same to that with 3.0 mmol of the catalyst.
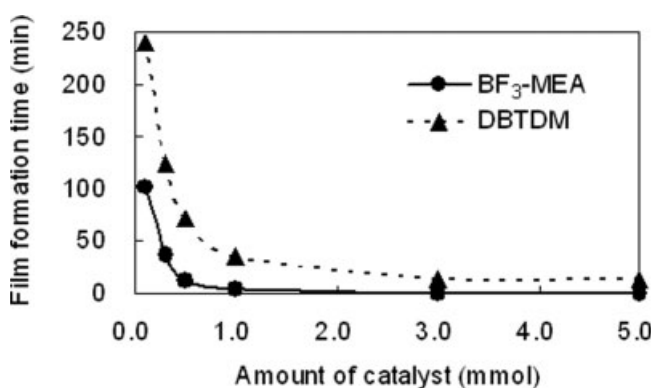

Figure 4 Film formation time of **3a** with different amounts of the catalyst (BF$_3$-MEA or DBTDM).
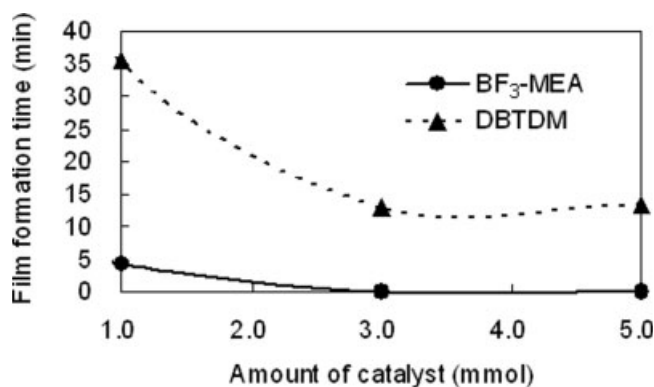
Figure 5 Higher magnification figure taken from the area between 1.0 and 5.0 mmol of the catalyst in Figure 4.

Figure 7 Higher magnification figure taken from the area between 2.5 and 10.0 mmol of the catalyst in Figure 6.

Comparison of curing speed between BF₃-MEA and DBTDM in the presence of aminosilane

In the moisture-curable adhesives, aminosilane compounds [e.g., 3-aminopropyltrimethoxysilane or N-(2-aminoethyl)-3-aminopropyltrimethoxysilane] were usually employed as the adhesion promoter, especially to improve the adherence to metals. The aminosilanes have the effect on not only the promotion of the adherence but also the acceleration of the curing speed. To confirm the curing speed in the presence of aminosilane and catalyst (BF₃-MEA or DBTDM) at the same time, 3-aminopropyltrimethoxysilane (2.5 g, 5.0 g, and 10 g) was added to the mixture of 100 g of **3a** and 0.1 mmol of BF₃-MEA or DBTDM, respectively. Figure 6 shows the film formation time of **3a** with the adhesion promoter (0–10 g of 3-aminopropyltrimethoxysilane), and Figure 7 is the magnification of the area from 2.5 to 10 g. In both cases, the film formation time became significantly faster. In particular, the curing speed was very fast in the case with BF₃-MEA.
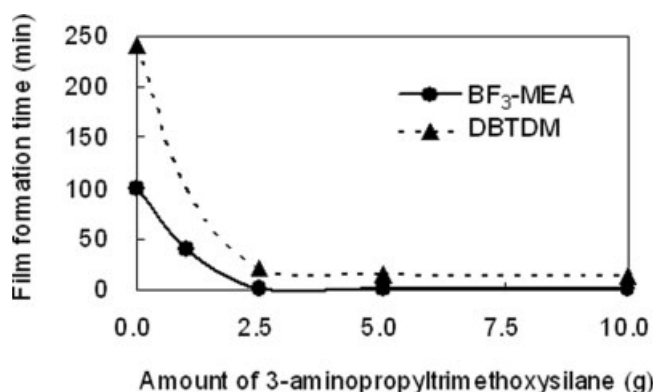
Comparison of curing speed of adhesives between BF₃-MEA and DBTDM

The curing speed of **4a** (catalyst: BF₃-MEA) and **4b** (catalyst: DBTDM) was evaluated as the film formation time (Table I). DBTDM is one of the highest-active curing catalysts of alkoxysilyl groups. However, the film formation time of **4a** was faster than that of **4b**, as shown in Table I, indicating that BF₃-MEA is obviously higher-active curing catalyst than DBTDM. There are two possible reasons, which involve different condensation mechanism of alkoxysilyl group and difference in the strength of Lewis acidity. Van der Weij reported a possible condensation mechanism with organotin compound (Scheme 2).[23] The condensation mechanism with DBTDM applied in this study is considered to follow the mechanism shown in Scheme 2. Scheme 3 shows a postulated mechanism with BF₃-MEA. BF₃ is known to be a strong oxophilic Lewis acid.[31] Although BF₃-MEA is expected to have less Lewis acidity in comparison with BF₃, BF₃-MEA is generally employed as a curing catalyst for epoxy resin.[27–29] In other words, BF₃-MEA has the oxophilicity enough for complexation with oxygen atom. In both mechanisms, the trigger of the condensation is H₂O, which is moisture in the air. In the case of the reaction with DBTDM, the conversion from —SnOCH₃ to —SnOH is necessary before the catalytic cycle. In contrast, BF₃-MEA is interacted with —Si—O—R beforehand, and the catalytic cycle could start immediately after encounter-

Figure 6 Film formation time of **3a** in the presence of the adhesion promoter (3-aminopropyltrimethoxysilane) and catalyst (BF₃-MEA or DBTDM).
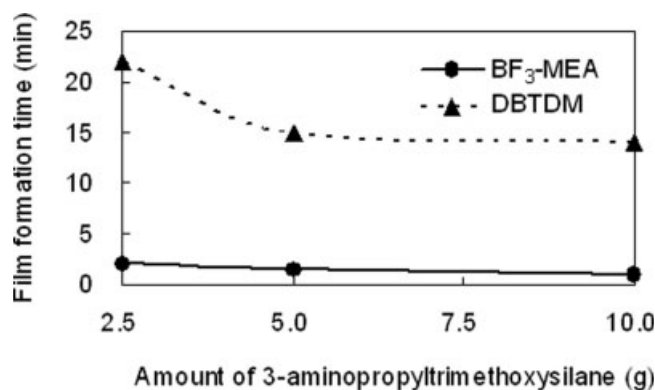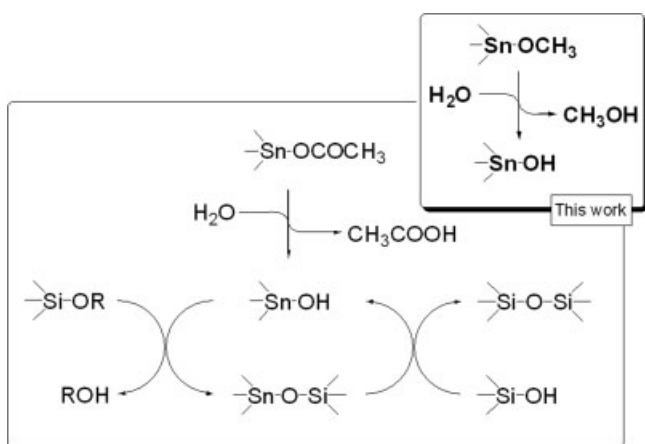
TABLE I
Film Formation Time of 4a and 4b

	Film formation time (s)
4a[a]	20
4b[b]	180

[a] BF₃-MEA.
[b] DBTDM.

Scheme 2 Catalytic cycle of organotin methoxide catalyst.[23]

Figure 8 Physical properties of **4a** (catalyst: BF_3-MEA) and **4b** (catalyst: DBTDM).

ing with H_2O. Moreover, BF_3-MEA is a very strong Lewis acid, which should accelerate the catalytic cycle. Both factors may affect efficiently on the curing process of the silylated polyurethanes in the presence of BF_3-MEA.

Comparison of physical property of cured adhesives between BF_3-MEA and DBTDM

The tensile strength at break, elongation at break, 100% modulus, and 50% modulus of **4a** (catalyst: BF_3-MEA) and **4b** (catalyst: DBTDM) were evaluated to confirm the physical properties of the adhesives. As shown in Figure 8, all data including the tensile strength at break, elongation at break, 100% modulus, and 50% modulus of **4a** (catalyst: BF_3-MEA) were lower than those of **4b** (catalyst: DBTDM). The result may be due to the fact that BF_3-MEA acts simply as a catalyst for the crosslinking reaction, whereas DBTDM may be partly incorporated in the crosslinkage, like Si—O—Sn—O—Si. As a result, in the case of DBTDM, the adhesive based on silylated polyurethane should be harder but more brittle than that in the case of BF_3-MEA.

Comparison of bond strength between BF_3-MEA and DBTDM

The tensile shear bond strengths of **4a** (catalyst: BF_3-MEA) and **4b** (catalyst: DBTDM) were evaluated to confirm the capability of BF_3-MEA as a curing catalyst of the adhesives. As shown in Figure 9, no significant difference was observed in the bond strengths between **4a** and **4b**.

Comparison of heat resistance between BF_3-MEA and DBTDM

The heat resistances in the tensile shear bond strengths of **4a** (catalyst: BF_3-MEA) and **4b** (catalyst: DBTDM) were evaluated. Figure 10 shows that better heat resistance was obtained with the adhesive prepared with BF_3-MEA, compared to that with DBTDM. When the heat resistance test was conducted at 80 and 105°C for 1 week, the bond strength of the adhesive obtained with BF_3-MEA maintained without deterioration, whereas the bond strength of the adhesive with DBTDM was deteriorated apparently. The deterioration might be attributed to the decomposition of the urethane
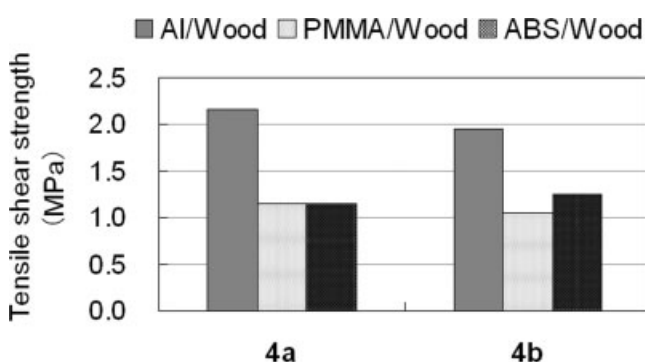

Scheme 3 A postulated catalytic cycle of BF_3-amine complex catalyst.

Figure 9 Tensile shear strength of **4a** (catalyst: BF_3-MEA) and **4b** (catalyst: DBTDM).
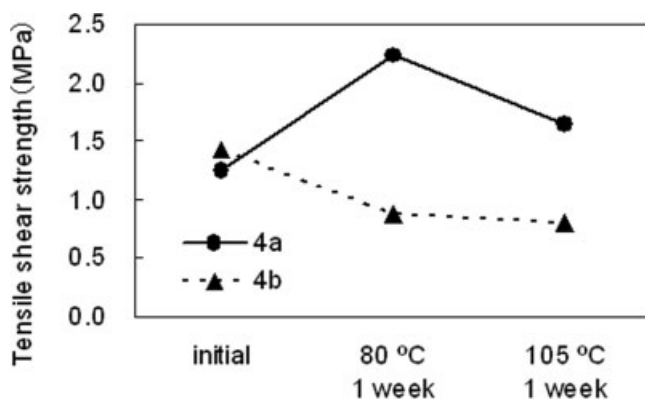
Figure 10 Heat resistance in tensile shear strength of **4a** and **4b**.

groups in the silylated polyurethane by organotin compound, which was a matter of concern for silylated polyurethanes in the past studies.[32] BF_3-MEA was found to be an effective catalyst with high catalytic activity without decomposition of the urethane groups. This result is worthy of special mention, because the organotin compound with high catalytic activity led generally to the remarkable decrease in the bond strength in the heat resistance test.

The reason for the increase in the strength at 80°C for 1 week compared with initial one may be due to the reaction progress by heating, while the decrease in the strength at higher temperature (105°C for 1 week) is considered to be attributed to the decomposition of the poly(propyleneoxide) segment in the main chain by oxidization due to high temperature.[33] Hence, heat stabilizers are necessary for the achievement of higher heat resistance.

SUMMARY

In this study, we found that BF_3-MEA acted as an efficient catalyst for the silylated polyurethane having moisture curable property. The bond strength of the adhesives prepared with BF_3-MEA was almost the same as the one used with DBTDM. On the other hand, BF_3-MEA was superior to DBTDM in terms of the curing speed and the heat resistance. BF_3-MEA can be successfully employed for the preparation of one-component solvent-free elastic adhesives, especially for the adhesives based on silylated polyurethane.

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