Properties of Polyurethane Coatings Containing Additives of Phenolic Compounds

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ABSTRACT: The properties of polyurethane containing five kinds of model phenolic additives were investigated. The IR spectra of polyurethane containing phenolic additives indicated that the phenolic additives reacted with isocyanate groups in a polyisocyanate compound. For an index of anticorrosion, the tensile adhesion strength was measured for polyurethane coatings with phenolic additives on steel plates treated with the salt-water spraying test for 3000 h. It was found that there was a relationship between the tensile adhesion strength of polyurethane and the density. We considered the reason to be that the increase in density (i.e., a reduction in free volume) should provide a route to reduce salt-water access to an adhesive bond. The increase in density was explained by the term antiplasticizers, which means that the phenolic additives reduce the free volume that is available for molecular motion in the stiff chain of polyurethane. In the polyurethanes with every phenolic additive, the elongation was increased, the moduli were decreased, the storage modulus was decreased, and the coefficient of thermal expansion was increased. These phenomena are the characteristics of plasticizers. Thus, the phenolic additives have both the character of antiplasticizers and plasticizers, but the polyurethane with phenolic additives had more characteristics of plasticizers than those of antiplasticizers. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2099–2106, 2006

Key words: polyurethane; phenolic compounds; additives; coatings; anticorrosion; antiplasticizers; plasticizers; adhesion; free volume; density

INTRODUCTION

Polyurethane is a reaction product of polyol with polyisocyanate and it has been applied for various adhesives, coatings, urethane foams, and so on.[1] For contact adhesives in the footwear and automotive industries, the properties of thermoplastic polyurethanes with different hard/soft segment ratios containing rosin as additives were recently investigated; it was found that rosin modifies the degree of phase separation and the miscibility of the hard and soft segments in the polyurethane chains, and then the initial adhesion to poly(vinyl chloride) is enhanced.[2]

Tar–urethane coatings have been used for heavy-duty anticorrosive coatings for many years.[3] Coal tar has been added to anticorrosive additives because of good anticorrosion and good economy.[4–13] However, recently, because of carcinogenicity, the difficulty in checking because of black or dark brown color, and tightening of environmental pollution laws, a need has arisen to change to a nontar system.[14–16] Some researchers have focused their attention on substitution additives for coal tar. For example, modified aromatic petroleum resins,[17] pigments (zinc white, alumina, iron oxide) prepared with optimum volume concentration,[14] coumarone–in-dene resins or petroleum resins,[18] and reaction products of xylene–formaldehyde resins with epoxy resins[19] were proposed for substitution additives.

Substitution additives were also investigated.[20–24] In order to find which components in coal tar are effective for anticorrosion, the properties of polyurethane containing some polycyclic aromatic compounds for model coal tar components were studied. We found that anticorrosion of the systems containing 2-naphthol (2-Np) for one of the model coal tar components was improved.[20] Other phenolic additives were studied and their improvement in anticorrosion was also found.[25,26] Poly(isopropylidene-phenol), which is a byproduct in industrial production systems of bisphenol A, and a polycondensation oligomer of creosote oil, in which phenolic compounds are contained, with formaldehyde were studied for examples of other phenolic additives. However, in these previous studies, the relationship between anticorrosion and the properties of polyurethane containing the above phenolic additives was not mentioned. Thus, we prepared model polyurethane coatings containing five kinds of model phenolic additives. Then we investigated the relationships between anticorrosion and the properties of the model polyurethane compounds. Phenol (Ph), 2-Np, 4-phenyl-phenol (4-ph-Ph), *p-tert*-buthyl-phenol (*p-t*Bu-Ph), and *p*-nonyl-phenol (*p*-C9-Ph) were used for the model phenolic additives. For an index of anticorrosion, the tensile adhesion strength of polyurethane coatings on steel plates, which were treated with the salt-water

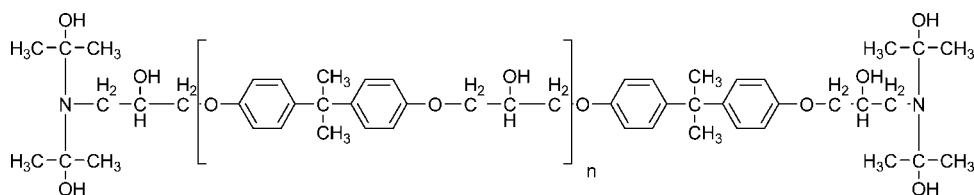*Correspondence to:* N. Yokoyama (yokoyaok@nscc.co.jp).

Figure 1 The molecular structure of polyol.

spraying test (SST) for 3000 h, was adopted. It is a general way to evaluate anticorrosion of coatings.[27] Furthermore, in this study the effects of model phenolic additives on the properties of polyurethane were considered in terms of plasticizers and antiplasticizers[28–32] or fortifiers.[33–41]

Although phenolic additives are not carcinogens, they are drastic medicines. According to Japanese law, phenolic compounds are defined as Class C in Harmful Liquid Materials. Although quantitative regulations for the effusion of phenolic compounds into the sea are not defined, their effusion into the sea is undesirable. In a previous study effusion tests of polyurethane coatings containing 2-Np in water were carried out at 23°C for 80 days.[20] As a result, effusion of 0.2% 2-Np by weight was found. Thus, we are now studying new phenolic additives that do not effuse into water.

For the polyol in this study a reaction product of diglycidyl ether of bisphenol A (DGEBA) and alcoholic diisopropanolamine (DIPA) was used,[25,26] which is epoxy polyol (DGEBA-DIPA). A reaction product of toluene diisocyanate (TDI) and trimethylol propane (TMP) was used for polyisocyanate (TDI-TMP). Generally, because of good anticorrosion and good economy, the combination of DGEBA-DIPA and TDI-TMP has been applied for heavy-duty anticorrosive coatings.[42,43]

EXPERIMENTAL

Materials

Polyol

DGEBA adducted with DIPA was used for the polyol (DGEBA-DIPA). Epotohto 128 (Tohto Kasei Co., Ltd.)

was used for DGEBA. A reagent produced by Jyunsei Chemical Co., Ltd., was used as the DIPA.

DGEBA (120 g) and solvent (204 g) were put into a 1-L separable flask and dissolved under mixing conditions. A mixture of toluene, methylisobutylketone (MIBK), and methylethylketone (MEK) with a weight ratio of 5 : 3 : 1 was used as a solvent. DIPA (84 g) was added and reacted at 80°C for 3 h. DGEBA and DIPA were mixed with an equivalent ratio of 1. DGEBA-DIPA was prepared for 50% solid content by weight. The molecular structure of DGEBA-DIPA is presented in Figure 1.

The characteristics of the polyol (DGEBA-DIPA) are presented in Table I. The hydroxyl groups in DGEBA-DIPA react with the isocyanate groups in TDI-TMP and then the polyurethane network was formed.

Polyisocyanate

A 75% by weight butyl acetate solution of TDI adducted with TMP (Takenate D-103H, Mitsui-Takeda Chemical Co., Ltd.) was used for polyisocyanate (TDI-TMP).

The molecular structure of TDI-TMP is presented in Figure 2 and the characteristics are presented in Table I. The isocyanate groups in TDI-TMP react with the hydroxyl groups in DGEBA-DIPA and the hydroxyl groups in the phenolic additives.

Additives

For model phenolic additives, five kinds of phenolic compounds were used: Ph, 2-Np, 4-ph-Ph, p-tBu-Ph, and p-C9-Ph, which are reagents produced by Kanto Chemical Co., Ltd. The characteristics of the phenolic additives are presented in Table I. The hydroxyl

TABLE I
Characteristics of Polyol, Polyisocyanate, and Phenolic Additives

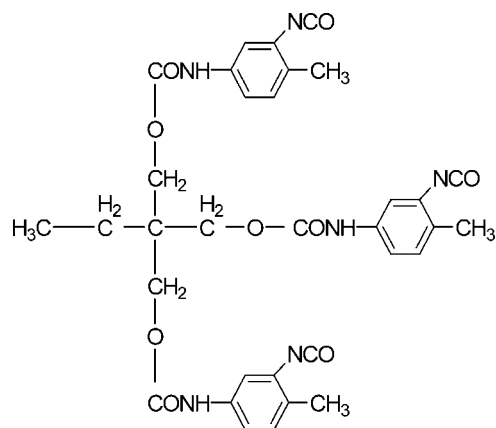| Components	Mol. wt	Equiv. wt of OH or NCO groups (g/eq)	Viscosity at 25°C (mPa s)
Polyol			
DGABA-DIPA	638	106	276 (50% solution)
Polyisocyanate			
TDI-TMP	640	242	4660 (75% solution)
Additives			
Phenol (Ph)	94	94	—
2-naphthol (2-Np)	144	144	—
4-phenyl-phenol (4-ph-Ph)	170	170	—
p-tert.-buthyl-phenol (p-tBu-Ph)	150	150	—
p-nonyl-phenol (p-C9-Ph)	220	220	—

Figure 2 The molecular structure of polyisocyanate.

groups in the phenolic additives react with the isocyanate groups in TDI-TPM, and then urethane bonds are formed. However, they do not form polyurethane networks (i.e., the phenolic additives might perform as internal additives).

Formulations

The formulations of polyurethanes containing our model phenolic additives are provided in Table II. Every formulation was prepared to be a 50% varnish by weight. A mixture of toluene, MIBK, and MEK with a weight ratio of 5 : 3 : 1 was used as a solvent. The equivalent ratios among polyol, polyisocyanate, and the model phenolic additives were 1 : 1 : 0, 1 : 1 : 0.1, 1 : 1 : 0.2, and 1 : 1 : 0.4, respectively.

Measurements

IR spectra

Resin varnishes (4.5 g), which were prepared according to Table II, were coated on two Teflon sheets (30 × 10 × 1 mm). The coated Teflon sheets were dried and cured for 2 weeks at 23°C and 65% relative humidity (RH). In this manner polyurethane films were prepared and used for samples. In order to judge the proceeding of the curing reaction, the absorption strengths at 2270 and 2940 cm^{-1} were measured and their ratio was calculated. Generally, the ratio of the absorption strength is known as an index of unreacted isocyanate groups in polyurethane.[44] Absorption at 2270 cm^{-1} is attributable to a stretching vibration of the isocyanate bond and that at 2940 cm^{-1} is attributable to a stretching vibration of the C—H bond for a standard. A Hitachi 270-50 apparatus was used as the IR spectrophotometer.

Density

Resin varnishes (100 g), which were also prepared according to Table II, were poured into a 300-mL poly-

TABLE II
Components and Properties of Polyurethane

	Ex.0	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Ex.6	Ex.7
Polyol								
DGEBA-DIPA	30.2	28.6	29.0	27.9	25.9	27.5	27.8	26.8
Polyisocyanate								
TDI-TMP	69.8	66.2	67.0	64.4	59.8	63.6	64.2	62.0
Additives								
Ph	0	5.2	0	0	0	0	0	0
2-Np	0	0	4.0	7.7	14.3	0	0	0
4-ph-Ph	0	0	0	0	0	8.9	0	0
p-tBu-Ph	0	0	0	0	0	0	8.0	0
p-C$_9$-Ph	0	0	0	0	0	0	0	11.2
Total (wt %)	100	100	100	100	100	100	100	100
Equiv. ratio of polyol/								
polyisocyanate/additives	1 : 1 : 0	1 : 1 : 0.2	1 : 1 : 0.1	1 : 1 : 0.2	1 : 1 : 0.4	1 : 1 : 0.2	1 : 1 : 0.2	1 : 1 : 0.2
Unreacted NCO groups[a]	28.9	8.3	20.2	11.2	2.1	14.0	6.1	11.0
Density × 10^{-3} (kg/m^3)	1.180	1.187	1.184	1.190	1.193	1.187	1.190	1.191
Tensile strength (MPa)	32.6	39.4	—	32.0	—	33.4	30.7	396.0
Elongation (%)	2.8	3.9	—	3.7	—	4.3	7.2	3.5
Moduli × 10^2 (MPa)	13.0	10.6	—	10.4	—	9.4	7.9	11.2
Storage modulus (GPa)								
23°C	2.7	2.5	—	2.4	—	2.1	2.1	2.3
170°C	0.012	0.016	—	0.014	—	0.012	0.012	0.014
T_g (°C)	122	106	—	104	—	104	110	108
Coefficient of thermal								
expansion (ppm)	152	178	—	173	—	180	176	178
Adhesion strength (MPa)								
Initial state	0.65	0.89	—	0.85	—	1.05	1.11	1.21
After SST	0.47	0.84	—	0.89	—	0.71	1.17	1.18

[a] The ratio of the absorption strength is ($v_{N=C=O}$ (2250 cm^{-1})/v_{C-H} (2920 cm^{-1})) × 100.

propylene cup, dried, and cured at 23°C and 65% RH for 2 weeks. Polyurethane sheets were prepared in polypropylene cups and used for samples. The density was measured in accordance with Japanese Industrial Standard (JIS) K 7112, which is equivalent to ISO 1183.

Tensile tests

Resin varnishes (45 g) in accordance with Table II were poured into a polypropylene tray (24 × 18 × 3 cm). The poured varnish was kept at 23°C and 65% RH for 2 weeks in order to prepare a polyurethane sheet. The polyurethane sheet was cut to the size of type 1 dog-bone specimens as described in JIS K 6251, which is equivalent to ISO 37 : 77. The dog-bone specimens were set on a tensile tester (Autograph AGS-500, Shimadzu Co., Ltd.); tensile tests were performed in accordance with JIS K 7161 (equivalent to ISO 527-1) at 23°C, 65% RH, and a crosshead speed of 1 mm/min. The tensile strength and elongation were measured, and the moduli of the polyurethanes were calculated with the Young equation.

Dynamic mechanical analysis (DMA)

The above polyurethane sheets cut to 5 × 30 mm were used for samples. A DMS 6100 (Seiko Instrument Co., Ltd.) was used as a DMA test machine. The storage modulus (E') and loss tangent (tan δ) were measured as a function of temperature over 20–200°C. The measurements were performed at a constant frequency of 10 Hz and a constant heating rate of 2°C/min. The E' in the rubbery plateau gives the information on the cross-linking densities of polyurethane, and the tan δ as a function of temperature gives the information on α dispersion (mobility of polyurethane chains) and the glass-transition temperature (T_g).

Thermal mechanical analysis (TMA)

TMA was performed to determine the coefficients of thermal expansion (α) of polyurethane at a constant heating rate of 2°C/min. Samples were prepared in the same way as DMA. A DMS 6100 (Seiko Instrument Co., Ltd.) was used as a TMA machine.

Curing rate

For an index of the initial curing rate of polyurethane, the viscosity of 50% by weight resin varnishes (Table II) was measured as a function of time at 25°C. An E-type viscometer (TOKIMEC Co., Ltd.) was used.

Tensile adhesion strength

Sandblasted steel plates (SS-41) were used for adherents. Barrages were made around the adherents by mounting two sheets of pressure-sensitive adhesive cloth tapes (no. 101, Nichiban Co., Ltd.) that were cut to 2-mm widths. For a sealant, a mixture of polyol and polyisocyanate was coated on the inside of the barrages. The sealant was cured for 24 h at 23°C and 65% RH. Resin varnishes (Table II) were poured into the inner sides of the barrages until the highest limit and dried for 24 h at 23°C and 65% RH. Then they were cured for 2 weeks at 23°C and 65% RH. The thickness of the polyurethane coatings was 100 μm.

The tensile adhesion strength was measured in accordance with ASTM D 4541. A circular jig made of aluminum with a cross-sectional area of 3.14 cm^2 was bonded with a polyurethane coating by using a commercial epoxy resin adhesive. For a pretreatment, an adhesion side of a circular jig was ground with sandpaper in order to prevent interfacial destruction between the jig and coating. The epoxy resin adhesive was cured at 23°C and 65% RH for 24 h. The polyurethane coating around the jig was cut with a circular saw joined with a drill. Samples were prepared in this manner. The samples were held to the lower chuck of a tension test machine (Autograph AGS-500, Shimadzu Co., Ltd.). The tension test machine was run at a crosshead speed of 10 mm/min in a controlled environment of 23°C and 65% RH. Measurements were performed at least 4 times and the average was adopted as the tensile adhesion strength.

SST

Because this polyurethane is mainly applied for heavy-duty anticorrosive coatings, a change of the tensile adhesion strength as a function of SST time was measured for an index of anticorrosion. The change of the tensile adhesion strength when treated by SST was measured for a general index of anticorrosion of coatings.[45] A Sugashikenki Co., Ltd. SST machine was used. The test conditions were a brine concentration of 5 wt %, an atmospheric temperature of 35°C, and a test time of 3000 h. The adhesion strength as a function of SST time was measured by picking samples out of the SST machine every week.

RESULTS AND DISCUSSION

Analysis of curing from IR spectra

The IR spectra of polyurethane without (Ex.0) and with (Ex.3) phenolic additives are presented in Figure 3. The absorption strengths at 2270 and 2940 cm^{-1} were measured, and the ratios (2270/2940 cm^{-1}) for an index of unreacted isocyanate groups was calculated. The results are presented in Table II. When the absorption strength ratio (2270/2940 cm^{-1}) is lower, there will be fewer unreacted isocyanate groups. Because the absorption strength ratio (2270/2940 cm^{-1}) in Ex.0 is
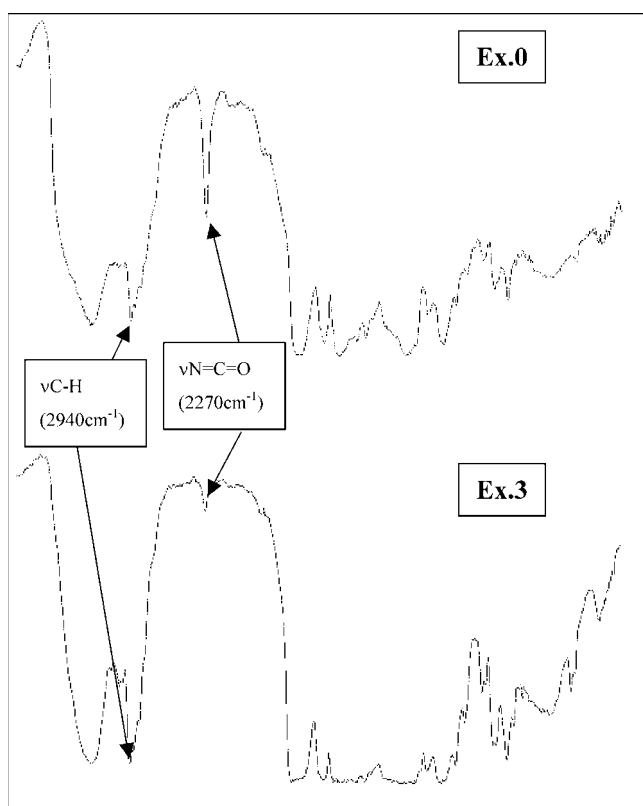
Figure 3 IR spectra of cured polyurethane without phenolic additives (Ex.0) and with 2-Np (Ex.3).

not zero, it could be that isocyanate groups still exist in Ex.0. When more 2-Np is added (Ex.0 → Ex.2 → Ex.3 → Ex.4), the absorption strength ratio (2270/2940 cm^{-1}) becomes lower. Possibly 2-Np reacted with residual isocyanate groups that did not react with polyol, and then 2-Np was integrated in the polyurethane system.

Density

The densities of polyurethane with and without the phenolic additives are presented in Table II. The deviations were within ±1%. The densities were increased by the presence of the phenolic additives. The increase of the density can be explained by the term antiplasticization.[28–30] The concept of antiplasticization is that the antiplasticizers of polar additives reduce the free volume that is available for molecular motion in the stiff chain of the above polymers. In terms of the free volume concept, when a small molecule (volume fraction V_1, fractional free volume f_1) is added to a polymer (volume fraction V_2, fractional free volume f_2), the free volume of the mixture is given by eq. (1)[46]:

$$f = V_1 f_1 + V_2 f_2 + K V_1 V_2 \tag{1}$$

where K is an interaction parameter. For most polymer/additive systems, K is generally negative but small (10^{-2}), and so the free volume of a polymer (low

f) is generally increased by the addition of a small (high f) molecule; hence, plastization occurs. The principle of antiplastization is that the resulting interaction parameter between the polymer and additive is negative and large. Then the free volume is decreased with the additive and the modulus increases. From the antiplastization, we considered that the phenolic additives perform for antiplasticizers and then the densities of polyurethane with them were increased.

Daly et al.[34] reported a similar phenomenon on amine-cured epoxy resin systems; the density of cured epoxy was increased by an additive of the reaction product of 1,2-epoxy-3-phenoxypropane (EPP) and 4-hydroxyacetanilide (HAA), which is EPPHAA.

Tensile tests

The tensile strength, elongation, and moduli of polyurethane are also presented in Table II. The deviations were within ±5%. The tensile strength of the systems with the phenolic additives changed a small amount or increased slightly as compared to that without the phenolic additives. The elongation was increased and the moduli were decreased by the phenolic additives. An increase in the tensile strength is a characteristic of antiplasticizers.[28–30] In contrast, an increase of the elongation is a characteristic of plasticizers. Because the tensile strength of polyurethane with the phenolic additives changed little or increased slightly, we considered that the phenolic additives might perform for plasticizers rather than antiplasticizers from the results of these tensile tests.

DMA

The E' data as a function of temperature are presented in Figure 4. Table II presents E' at 23 and 170°C. The E' data at 23°C were decreased by the phenolic additives. This should also be a confirmation that the phenolic additives perform as plasticizers. However, no difference was found in the E' data at 170°C (i.e., E' on the rubbery plateau). This should indicate that because all the crosslinking densities of polyurethane were the same, the plasticized effect was not caused by a decrease of the crosslinking densities of polyurethane; that is, it might be caused by the presence of the phenolic additives for plasticizers.

The tan δ data as a function of temperature are presented in Figure 5. The α relaxations of polyurethane with the phenolic additives were broader than those without them. We considered that the phenomenon was due to the existence of some inhomogeneity. Daly et al.[34] demonstrated that the α relaxation (T_g) of amine-cured epoxy resins with the additive of the product (EPPHAA) of EPP and HAA was broader than that without EPPHAA, and they also considered that the phenomenon is attributable to the existence of some inhomogeneity on a very small scale (100s of angstroms).
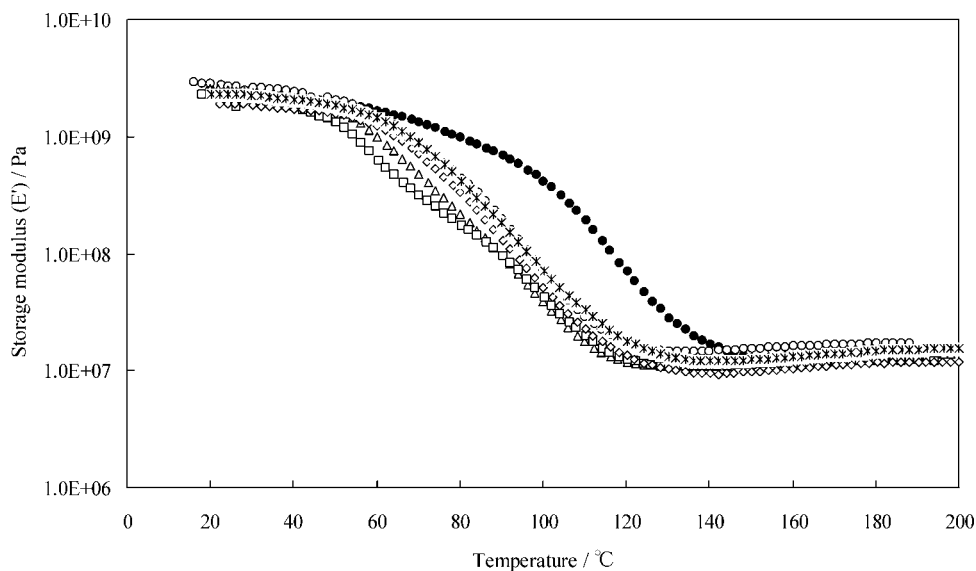
Figure 4 The relationship between the storage modulus (E') and temperature in the systems with and without phenolic additives: (●) Ex.0 (control), (○) Ex.1 (Ph), (△) Ex.3 (2-Np), (□) Ex.5 (4-ph-Ph), (◇) Ex.6 (*p-t*Bu-Ph), and (∗) Ex.5 (*p*-C9-Ph).

Coefficients of thermal expansion

The α values of the polyurethanes determined by TMA are also presented in Table II. Because the α of the polyurethanes was increased by the presence of the phenolic additives, we again confirmed that the phenolic additives perform as plasticizers.

Initial and post SST treatment tensile adhesion strengths for index of anticorrosion of coatings

The initial tensile adhesion strength of polyurethane coatings on steel plates and that treated with SST for 3000 h are provided in Table II. The deviations were within ±5% and, in all cases, interfacial destruction between polyurethane and adherents occurred.

The initial tensile adhesion strength of the systems with the phenolic additives was higher than that without them. We considered the reason to be in terms of the plasticizers of the phenolic additives; that is, when polyurethane is too rigid, high adhesion strength will not be obtained and the destruction mode will be interfacial because the molecular mobility of polyurethane will not be able to follow the deformation rate. When the phenolic additives for plasticizers are contained in polyurethane, the adhesion strength will become higher because the molecular mobility of polyurethane can follow the deformation rate. However, when the
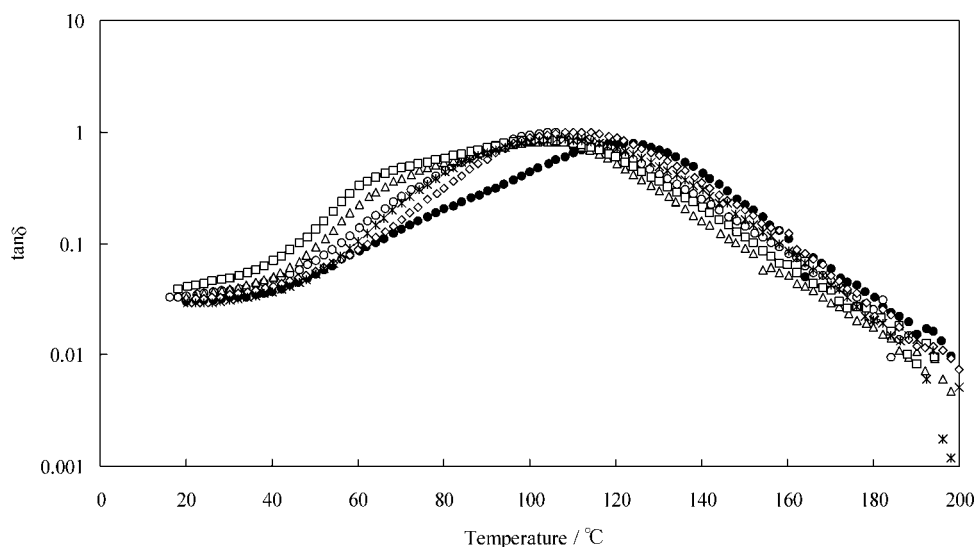

Figure 5 The relationship between the loss tangent (tan δ) and temperature in the systems with and without phenolic additives: (●) Ex.0 (control), (○) Ex.1 (Ph), (△) Ex.3 (2-Np), (□) Ex.5 (4-ph-Ph), (◇) Ex.6 (*p-t*Bu-Ph), and (∗) Ex.5 (*p*-C9-Ph).
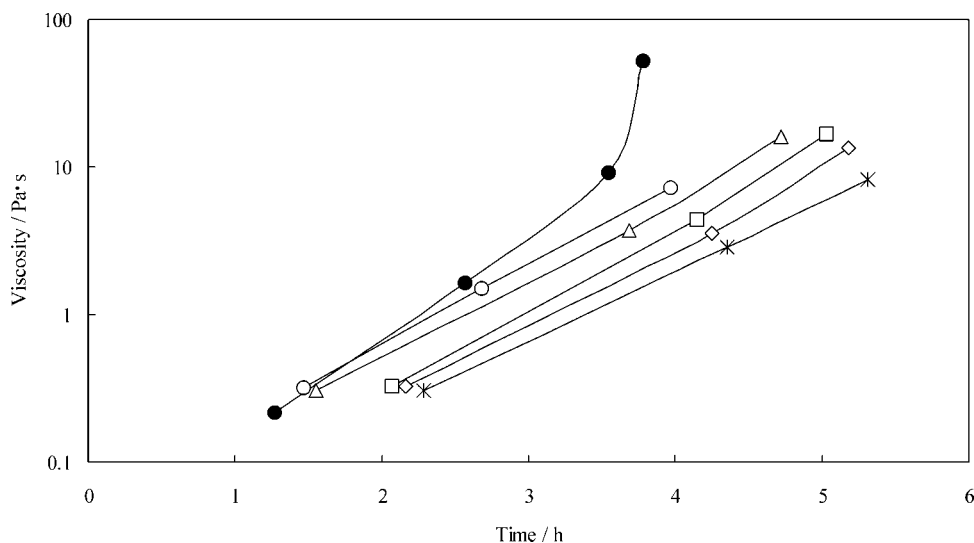
Figure 6 The relationship between the viscosity and time in the varnish systems with and without phenolic additives: (●) Ex.0 (control), (○) Ex.1 (Ph), (△) Ex.3 (2-Np), (□) Ex.5 (4-ph-Ph), (◇) Ex.6 (*p-t*Bu-Ph), and (∗) Ex.5 (*p*-C9-Ph).

polyurethane is too soft, high adhesion strength cannot be obtained because the molecular cohesion of polyurethane will become low and then the destruction mode will change to a cohesive mode. Thus, when the phenolic additives plasticize polyurethane in a reasonable way, the tensile adhesion strength of polyurethane will be increased.[47]

After the SST, the tensile adhesion strength of polyurethane containing 2-Np, *p-t*Bu-Ph, and *p*-C9-Ph was higher than that of the other. Furthermore, a relationship between the tensile adhesion strength when treated with SST and the density of polyurethane in the initial states was found; that is, as the density of polyurethane was higher, the tensile adhesion strength after SST was also higher. We considered the reason that an increase in density (i.e., a reduction in free volume) might provide a route to reducing salt-water access to an adhesive bond.[39]

Curing rate

For an index of the initial curing rate of polyurethane, the viscosities of the 50% by weight resin varnishes presented in Table II as a function of time are provided in Figure 6. Every varnish with the phenolic additives was lower than that without them when they are compared at same time. Thus, we found that the phenolic additives decelerated the initial curing rate of polyurethane. We considered that the reason was because of the characteristics of the phenolic additives for acid. It is generally known that the cure of polyurethane is decelerated by the presence of an acid compound.[48]

As shown in Figure 4, although the initial curing rate of polyurethane containing the phenolic additives was decelerated, there was no difference in the final crosslinking density of polyurethane.

CONCLUSIONS

1. From the IR spectra of polyurethane, every kind of model phenolic additives (Ph, 2-Np, *p-t*Bu-Ph, and *p*-C9-Ph) reacted with isocyanate groups in polyisocyanate. Thus, they might be integrated into polyurethane network systems as internal additives.
2. From the results of the tensile adhesion strength after SST, anticorrosion of polyurethane was improved by the presence of the phenolic additives. The effect of 2-Np, *p-t*Bu-Ph, and *p*-C9-Ph was especially better than the others. Furthermore, a relationship was found between the tensile adhesion strength after SST and the initial density of polyurethane containing the phenolic additives.
3. Although the phenolic additives indicated the combined characters of antiplasticizers and plasticizers, because the phenolic additives showed more characteristics for plasticizers than characteristics for antiplasticizers, they should be regarded as plasticizers rather than antiplasticizers.
4. Although the phenolic additives decelerated the initial curing rate in the crosslinking reaction of polyurethane, there was no difference in the final crosslinking density of every polyurethane system.

References

1. Iwata, K. Polyurethane Handbook; Nikkankogyoshinbunsha: Tokyo, 1986; p 2.
2. Aran-Ais, F.; Torro-Palau, A. M.; Orgiles-Barcelo, A. C.; Martin-Martinez, J. M. J Adhes Sci Technol 2002, 16, 1431.

3. Iwata, K. Polyurethane Handbook; Nikkankogyoshinbunsha: Tokyo, 1986; p 914.

4. Kozakiewicz, J.; Orzechowski, A.; Igielska, B.; Barbara, L.; Andrzej, C.; Turon, J.; Krowicka, I.; Lubczynska, E.; Wlazlo, A. Pol. Pat. 145,505, 1988.

5. He, S. Tuliao Gongye Chin 1982, 69, 14.

6. Bogs, H. J. 3R Int 1990, 29, 620.

7. Singh, S. M. Paintindia 1984, 34(7), 23.

8. Capeller, L. Presented at the 15th Fatipec Congress, 1980.

9. Ribei, B. Farbe Lack 1977, 83, 701.

10. Sakai, Y.; Uehara, K.; Nemoto, A. Jpn. Pat. 44,009,479, 1969.

11. Bauer, J. A. U.S. Pat. 3,383,345, 1968.

12. Nicks, P. F. Brit. Pat. 1,104,442, 1968.

13. Hopper, T. R. U.S. Pat. 3,331,795, 1967.

14. Jurgen, S.; Manfred, B. Farbe Lack 2001, 107(5), 84.

15. N. Kano, M. Hama, S. Inomata, Res Coat Jpn 1997, 129, 78.

16. Brinder, G. Mater Corrosion 2001, 52, 261.

17. Hama, M. JETI Jpn 1997, 45(14), 54.

18. Wang, Q.; Zhang, Z. Chin. Pat. 1,174,865, 1998.

19. Yamagishi, K. Jpn. Pat. 2,000,026, 769, 2000.

20. Yokoyama, N.; Fujino, K. JCT Res 2005, 2, 445.

21. Yokoyama, N. J Jpn Arom Ind Assoc 2003, 55, 139.

22. Yokoyama, N.; Fujino, K. J Adhes Soc Jpn 2003, 39, 100.

23. Yokoyama, N.; Fujino, K.; Kido, H. Jpn. Pat. 1,997,194,563, 1990.

24. Yokoyama, N.; Fujino, K. Jpn. Pat. 20,002,819,40A, 2000.

25. Yoshida, M.; Fujino, K.; Kido, H. Jpn. Pat. 1,997,194,563, 1997.

26. Fujino, K.; Yoshida, M. Jpn. Pat. 2,001,198,99A, 2001.

27. Ueda, K.; Kanai, H.; Furukawa, H.; Kimata, Y. Tech Report Nippon Steel Jpn 2002, 377, 25.

28. Jackson, W. J., Jr.; Caldwell, J. R. Adv Chem Ser 1965, 48, 185.

29. Jackson, W. J., Jr.; Caldwell, J. R. J Appl Polym Sci 1967, 11, 211.

30. Jackson, W. J., Jr.; Caldwell, J. R. J Appl Polym Sci 1967, 11, 227.

31. Wyzgoski, M. G.; Yeh, G. S. Y. Polym J 1973, 4, 29.

32. Hata, N.; Yamauchi, R.; Kumanotani, J. J Appl Polym Sci 1973, 17, 2173.

33. McLean, P. D.; Scott, R. F.; Garton, A. Br Polym J 1983, 15, 66.

34. Daly, J.; Britten, A.; Garton, A. J Appl Polym Sci 1984, 29, 1403.

35. McLean, P. D.; Garton, A.; Scott, R. F.; Gransden, S. E. U.S. Pat. 4,480,082, 1984.

36. McLean, P. D.; Scott, R. F. U.S. Pat. 4,739,028, 1988.

37. McLean, P. D.; Garton, A.; Stevenson, W. T. K.; MacPhee, K. E. Polym Compos 1986, 7, 330.

38. Garton, A.; McLean, P. D.; Stevenson, W. T. K.; Clark, J. N.; Daly, J. H. Polym Eng Sci 1987, 27, 1620.

39. Garton, A.; Haldankar, G. S. J Adhes 1989, 29, 13.

40. Mijovic, J. J Appl Polym Sci 1990, 40, 845.

41. Scott, R. F.; Lee, S.; Poon, C.; Gaudert, P. C. Polym Eng Sci 1991, 31, 1310.

42. Fujino, K.; Yoshida, M. Jpn. Pat. 2,001,198,99A, 2001.

43. Yoshida, M. Jpn. Pat. 20,011,150,78A, 2001.

44. Sato, N.; Nakamura, T.; Inagaki, S.; Yamada, E. J Adhes Soc Jpn 2001, 37, 101.

45. Hayano, S. Toso Kogaku Jpn 1999, 34(4), 116.

46. Ferry, J. D. Viscoelastic Properties of Polymers; Wiley: New York, 1970.

47. Hatano, Y.; Tomit, B.; Mizumachi, H. J Jpn Wood Res Soc 1983, 29, 578.

48. Mito, M. Technol Adhes 1996, 15, 1.