Properties of Polyurethane Containing New Phenolic Additives

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ABSTRACT: For non-tar anticorrosive polyurethane coatings, polyurethane containing phenolic additives (i.e., phenol, styrene adducts with phenol ([St]ₙ-Ph) and indene adducts with phenol ([In]ₙ-Ph) ) were prepared and the effusion properties were investigated. For an index on the effusion, the weight change of the polyurethane sheets soaked in water as a function of the soaking time and total organic carbon (TOC) in the water used for the soaking tests were measured. Only the weight of the polyurethane sheet containing [In]ₙ-Ph did not decrease during the soaking test and the TOC was the least. Furthermore, we investigated the properties of the phenolic additives plasticizers or “antiplasticizer”. Although the density and the coefficient of thermal expansion of polyurethane containing [In]ₙ-Ph were increased, since the tensile strength decreased and the elongation increased, [In]ₙ-Ph would be regarded as a plasticizer rather than “antiplasticizer”.

KEY WORDS: polyurethane, additives, phenolic additives, anticorrosive coatings, non-tar, effusion, plasticizers, antiplasticizers.

INTRODUCTION

Polyurethane is a reaction product of polyol with polyisocyanate and it has been applied for various adhesives, coatings, urethane foams, etc.¹ Recently, for contact adhesives in footwear and automotive industries, the properties of thermoplastic polyurethane with different hard/soft segment ratios containing rosin as additives were investigated and 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 PVC is enhanced.²

For heavy-duty anticorrosive coatings, tar-urethane coatings have been used for a long time.³ Coal tar has been added for anticorrosive additives because of the good anticorrosion and the good economy.⁴⁻¹³ But, recently, because of the carcinogenicity and tightening of environmental pollution laws, a need arisen to change to a non-tar
Therefore, some researchers have focused their attention on substitution additives for coal tar. Examples include, modified aromatic petroleum resins, some kinds of pigments (i.e., zinc white, alumina, iron oxide), coumarone-indene resin or petroleum resin, and reaction products of xylene-formaldehyde resin with epoxy resins.

The current authors have also investigated the substitution additives to find what components in coal tar are effective in enhancing anticorrosion. The properties of polyurethane containing some polycyclic aromatic compounds for model coal tar components were studied. It was found that anticorrosion of the polyurethane was enhanced by addition of the phenolic additives of phenol, 2-naphthol, etc. Although the above phenolic additives are not carcinogens, they are considered hazardous. On “Law Relating to the Prevention of Marine Pollution and Maritime Disaster in Japan”, the phenolic compounds are defined as “Class C in Harmful Materials”. Although quantitative regulations for the effusion of phenolic compounds into the sea are not defined, much effusion of them into the sea is not favorable. In our previous studies, on the polyurethane coatings containing 2-naphthol, the tests of effusion into water were carried out at 23 °C for 80 days, as the results, it was found that a 0.2% with a weight of 2-naphthol effused into water.

The objective of this work is to develop new “anti-effusive” phenolic additives for polyurethane anticorrosive coatings and to consider the properties of the new “anti-effusive” phenolic additives in the terms of “antiplasticizer” (or “fortifier”) and plasticizer. We described here the properties of 3 kinds of phenolic additives, i.e., phenol, styrene adducts with phenol ([St]n-Ph) and indene adducts with phenol ([In]n-Ph), on polyurethane coatings.

For polyol, polyetherpolyol was used, and for polyisocyanate, polymeric-MDI was used. Generally, the combination of polyetherpolyol and polymeric-MDI has been applied for heavy-duty anticorrosive coatings.

**EXPERIMENTAL**

**Synthesis of Styrene Adducts with Phenol ([St]n-Ph) and Indene Adducts with Phenol ([In]n-Ph)**

**Materials**

Styrene and indene, which is a production of Nippon Steel Chemical Co., Ltd., Japan respectively, were used as received. For a solvent, toluene, which is also a production of Nippon Steel Chemical Co., Ltd, Japan, was used as received. For a catalyst, p-toluene-sulfonic-acid, which is a reagent of Kanto Chemical Co., Ltd., Japan, was used as received.
Method

In accordance with Table 1, phenol, p-toluene-sulfonic-acid and toluene was put into a 200ml flask with 4 side tubes respectively. A 50% with a weight toluene solution of styrene or indene was added dropwise to a 200ml flask with a syringe respectively over 1h. After that, the reaction was performed at 85℃ for 1h. Then, calcium hydroxide was added in order to neutralize p-toluene-sulfonic-acid. The neutralization reaction was carried out at 85℃ for 15 minutes. And then, the neutralized product and extra calcium hydroxide were filtered off. Finally, the filtered solutions were evaporated in vacuo at 200℃. Thus, [St]_n-Ph and [In]_n-Ph were obtained. The synthesis scheme is presented in Figure 1.

| Table 1 | Synthesis conditions of [St]_n-Ph and [In]_n-Ph. |
| Initial components of monomer [mol%] | Initiator | Solvent | Temp. | Time | Conversion | Equivalent weight of hydroxyl groups |
| Styrene | Indene | Phenol | p-Toluene-sulfonicacid | Toluene | 85 | 1 | 95.3 | 241 |
| [St]_n-Ph | 50 | 0 | 50 | p-Toluene-sulfonicacid | Toluene | 85 | 1 | 93.6 | 267 |

**Figure 1**  Synthesis scheme of [St]_n-Ph and [In]_n-Ph.
Preparations of Polyurethane

Materials

For polyisocyanate, “Coronate 1130”, which is a polymeric-MDI produced by Nippon Polyurethane Industrial Co., Ltd., Japan, was used as received. The content of isocyanate groups in “Coronate 1130” is 31% with a weight, the viscosity is 109mPa•s at 25℃ and the molecular structure is presented in Figure 2.

For polyol, “G-300”, which is a polyether-polyol produced by Asahi Electrochemical Co., Ltd., Japan, was used as received. The value of hydroxyl groups in “G-300” is 511mgKOH/g, the viscosity is 560mPa•s at 25℃ and the molecular structure is also presented in Figure 2.

For a solvent, a mixture of toluene produced by Nippon steel Chemical Co., Ltd., Japan, methyl-isobutyl-ketone of a reagent and methyl-ethyl-ketone of a reagent was used respectively as received. The mixture ratio with a weight was 5:3:2.

【Figure 2】 Molecular structures of polyisocyanate and polyol.

![Molecular structure of polyisocyanate](image1)

![Molecular structure of polyol](image2)

Figure 2  Molecular structures of polyisocyanate and polyol.
Method

In accordance with Table 2, above polyol, polyisocyanate, phenolic additives and solvent were put into a 300ml disposable cup and they were mixed. A 200g of the mixtures was poured into a polypropylene tray. Then, they were dried and cured at 23 ℃ -65RH% for 21 days. Thus, polyurethane sheets were prepared for samples.

【Table2】 Formulations for polyurethane and the properties.

<table>
<thead>
<tr>
<th>Formulations</th>
<th>Ex.0</th>
<th>Ex.1</th>
<th>Ex.2</th>
<th>Ex.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>[% with a weight]</td>
<td>Polyol</td>
<td>22.4</td>
<td>18.1</td>
<td>16.7</td>
</tr>
<tr>
<td>Polyisocyanate</td>
<td>27.6</td>
<td>28.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Additives</td>
<td>Ph</td>
<td>0.0</td>
<td>3.9</td>
<td>0.0</td>
</tr>
<tr>
<td>[St]-Ph</td>
<td>0.0</td>
<td>0.0</td>
<td>7.5</td>
<td>0.0</td>
</tr>
<tr>
<td>[In]-Ph</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>8.0</td>
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<tr>
<td>Solvent</td>
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<td>50.0</td>
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<td>Total</td>
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<td>NCO/OH ratio by mol</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Properties</th>
<th>Ex.0</th>
<th>Ex.1</th>
<th>Ex.2</th>
<th>Ex.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial State [MPa]</td>
<td>0.58</td>
<td>0.65</td>
<td>0.73</td>
<td>0.63</td>
</tr>
<tr>
<td>After SST [MPa]</td>
<td>0.32</td>
<td>0.35</td>
<td>0.31</td>
<td>0.58</td>
</tr>
<tr>
<td>TOC [g/m³]</td>
<td>98.6</td>
<td>957</td>
<td>154</td>
<td>68.3</td>
</tr>
<tr>
<td>Density [kg/m³]</td>
<td>1.09</td>
<td>1.16</td>
<td>1.16</td>
<td>1.13</td>
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<tr>
<td>DMA</td>
<td>E' at 23 ℃ [GPa]</td>
<td>1.40</td>
<td>0.672</td>
<td>0.672</td>
</tr>
<tr>
<td></td>
<td>E' at 90 ℃ [GPa]</td>
<td>0.00828</td>
<td>0.00700</td>
<td>0.00700</td>
</tr>
<tr>
<td></td>
<td>Tg [℃]</td>
<td>52</td>
<td>52</td>
<td>44</td>
</tr>
<tr>
<td>TMA</td>
<td>α₁ (&lt;Tg) [ppm]</td>
<td>376</td>
<td>274</td>
<td>1080</td>
</tr>
<tr>
<td></td>
<td>α₂ (&gt;Tg) [ppm]</td>
<td>142</td>
<td>119</td>
<td>128</td>
</tr>
<tr>
<td>Tensile Test</td>
<td>Tensile Strength [MPa]</td>
<td>6.7</td>
<td>13.6</td>
<td>4.13</td>
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<tr>
<td></td>
<td>Elongation [%]</td>
<td>51.4</td>
<td>94.4</td>
<td>102.5</td>
</tr>
</tbody>
</table>
Measurement

Characterization of \([\text{St}]_n\)-Ph and \([\text{In}]_n\)-Ph

Molecular structures of \([\text{St}]_n\)-Ph and \([\text{In}]_n\)-Ph were characterized with \(^{13}\text{C}\)-NMR, \(^1\text{H}\)-NMR and Gas Chromatograph-Mass Spectrometer (GC-MS). For a measurement machine for \(^{13}\text{C}\)-NMR and \(^1\text{H}\)-NMR, “JNM-LA400” produced by Nippon Denshi Co., Ltd., Japan, was used. GC-MS was measured with “6890N” (for a GC unit) and “5973N” (for a MS unit) produced by Agilent Co., Ltd., U.S. respectively.

An equivalent weight of hydroxyl groups of \([\text{St}]_n\)-Ph and \([\text{In}]_n\)-Ph was measured in accordance with Japanese Industrial Standard (JIS) K 0070 that is equal to ICS 71.040.40.

Reaction Proceedings of Polyurethane

In order to analyze the reaction proceedings of polyurethane, the typical N=C=O bands (located on 2270 cm\(^{-1}\)) of isocyanate groups was detected by FT-IR spectra.\(^{41}\) The spectra were obtained in the transmission mode using “Spectram One” produced by Perkin-Elmer Co., Ltd., U.S.. For specimens, above polyurethane sheets were used.

Properties of Polyurethane

Soaking Tests in Water for Estimating Effusion Properties of Phenolic Additives

The polyurethane sheets described in above “Method” were cut to a size of 50mm×50mm and used for specimens. They were put into 300ml disposable cups with filling pure water and measured the changes of weight as a function of soaking time at 23℃-65 RH % for 46days.

After above soaking tests, total organic carbon (TOC) in the water was measured. For a TOC machine, “TOC-500” produced by Shimadzu Co., Ltd., Japan, was used.

Tensile Adhesion Strength as a Function of Salt-water Spraying Test (SST) time for an Index on Anticorrosion

Sandblasted steel plates, SS-41, were used for adherents. Barrages were made around the adherents by mounting 2 sheets of pressure-sensitive adhesive cloth tapes
(No.101, Nichiban Co., Ltd. Japan) that were cut to 2mm widths. For a sealant, a mixture of above polyol and polyisocyanate was coated on inside of barrages. The sealant was cured for 24h at 23℃-65RH%. Resin varnishes in accordance with Table 2 were poured into inner sides of the barrages until utmost limit and dried for 24h at 23℃-65RH% and then cured for 2 weeks at 23℃-65RH%. Thickness of polyurethane coatings was 100μm.

Tensile adhesion strength was measured in accordance with ASTM D 4541. A circular jig made of aluminum with a cross section area of 3.14cm² 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 a sand paper in order to prevent interfacial destruction between the jig and the coating. The epoxy resin adhesive was cured at 23℃-65RH% for 24h. The polyurethane coating around a jig was cut by a circular saw joined with a drill. In this manner, samples were prepared. The samples were held to a lower chuck of a tension test machine (“Autograph AGS-500” produced by Shimadzu Co., Ltd. Japan). The tension test machine was run at a crosshead speed of 10mm/min in a controlled environment of 23℃-65RH%. Measurements were performed 4 times at least and the average was adopted as tensile adhesion strength.

Since this polyurethane is applied for heavy-duty anticorrosive coatings, a change of tensile adhesion strength as a function of SST time was measured for an index on anticorrosion. The change of tensile adhesion strength of polyurethane coatings treated with SST is measured for a general index on anticorrosion of coatings. For a SST machine, a production produced by Sugashikenki Co., Ltd., Japan was used. The test conditions were as follows, i.e., brine concentration was 5% with a weight, atmosphere temperature was 35℃ and test time was for 3000h. Tensile adhesion strength as a function of SST time was measured by picking up samples in the SST machine every week.

**Density**

The polyurethane sheets were cut to a size of 5mm × 10mm and used. The densities were measured in accordance with JIS K 7112 that is equal to ISO 1183.

**Dynamic Mechanical Analysis (DMA)**

Polyurethane sheets cut to a size of 5mm × 30mm were used. For a DMA machine, “DMS 6100” produced by SEIKO Instrument Co., Ltd., Japan, was used. Storage modulus (E’) and loss tangent (tanδ) was obtained respectively at a constant frequency of 10Hz over the temperature range 20℃-200℃ at a constant heating rate of 2℃/min.
Thermal Mechanical Analysis (TMA)

In order to determine coefficients of thermal expansion of the polyurethane, TMA was measured at a constant heating rate of 2 °C/min. For a TMA machine, “DMS 6100” produced by SEIKO Instrument Co., Ltd. Japan, was also used. For specimens, above polyurethane sheets cut to a size of 5mm × 30mm were also used.

Tensile Tests

Polyurethane sheets cut to a dog-bone shape of Type 1 defined in JIS K 6251 equal to ISO 37:77 were used. They were set to a tensile tester (“Autograph AGS-500” produced by Shimadzu Co., Ltd., Japan), and the tensile strength and the elongation were measured. The tests were performed at least 4 times per data and the average was adopted. The tests were performed in a controlled environment (23 ±65RH%) at a constant crosshead speed of 1mm/min.

RESULTS AND DISCUSSION

Characterization of [St]_n-Ph and [In]_n-Ph

GC-MS data of [St]_n-Ph and [In]_n-Ph are presented in Figure 3. From the molecular weight, the peaks of ① and ② in [St]_n-Ph would correspond to two isomers of [St]_n=1-Ph, the peaks of ③, ④ and ⑤ would correspond to three isomers of [St]_n=2-Ph, and the peak of ⑥ would correspond to [St]_n=3-Ph.

While, the peaks of ①, ②, ③ and ④ in [In]_n-Ph would correspond to four isomers of [In]_n=1-Ph, the peak of ⑤ would correspond to indene dimer, the peaks of ⑥, ⑦ and ⑧ would correspond to three isomers of [In]_n=2-Ph, and the peak of ⑨ would correspond to [In]_n=3-Ph.
Figure 3  GC-MS charts of $[\text{St}]_n$-Ph and $[\text{In}]_n$-Ph.
$^{13}$C-NMR spectrum of [St]$_n$-Ph is presented in Figure 4. The assignation of every peak of “a”, “b”, “c” and “d” is also illustrated in Figure 4 respectively. From the ratio of “a”, “b”, “c” and “d” on integration of the every peak’s area, it was found that the styrene adducts with phenol at ortho position in phenol is 66.9% with a mol and the styrene adducts with phenol at para position in phenol is 33.1% with a mol.

【Figure 4】 $^{13}$C-NMR spectra of [St]$_n$-Ph.
$^{13}$C-NMR spectrum of $[\text{In}]_n$-Ph is presented in Figure 5. The assignation of every peak of “a”, “b”, “c”, “d” and “e” is also illustrated in Figure 5 respectively. From the ratio of “a”, “b”, “c” and “d” on integration of the every peak’s area, it was found that the indene adducts with phenol at ortho position in phenol is 60.7% with a mol and the styrene adducts with phenol at para position in phenol is 39.3% with a mol.

【Figure 5】 $^{13}$C-NMR spectra of $[\text{In}]_n$-Ph.
1H-NMR spectra of [St]_n-Ph is presented in Figure 6. The assignation of every peak of “a” and “b” is also illustrated in Figure 6 respectively. From the ratio of “a” and “b” on integration of the every peak’s area, it was found that the styrene adducts with phenol at ortho position in phenol was 67.0% with a mol and the styrene adducts with phenol at para position in phenol was 33.0% with a mol. The results agreed with the above result from 13C-NMR spectrum.

【Figure 6】 1H-NMR spectra of [St]_n-Ph.
$^1$H-NMR spectra of [In]$_n$-Ph is presented in Figure 7. The assignation of every peak of “a” and “b” is also illustrated in Figure 7 respectively. From the ratio of “a” and “b” on integration of the every peak’s area, it was found that indene adducts with phenol at α position in indene is 60.9% with a mol and indene adducts with phenol at β position in indene is 39.1% with a mol respectively.

Figure 7  $^1$H-NMR spectra of [In]$_n$-Ph.
From above results of GC-MS, $^{13}$C-NMR and $^1$H-NMR, the molecular structures of $[\text{St}]_n$-Ph and $[\text{In}]_n$-Ph were characterized. The results are presented in Table 3.

**Table 3**  Results of characterization on $[\text{St}]_n$-Ph and $[\text{In}]_n$-Ph.

<table>
<thead>
<tr>
<th>Components</th>
<th>$n$</th>
<th>Isomers [%] (by area of GC)</th>
<th>Molecular structures</th>
</tr>
</thead>
</table>
| $[\text{St}]_n$-Ph | $n=1$ | \[ \begin{array}{c}
\text{Isomer 1} \\
\text{Isomer 2} \\
\text{Isomer 3}
\end{array} \] | \[
\text{Structure 1} \\
\text{Structure 2} \\
\text{Structure 3}
\] |
| $n=2$ | \[ \begin{array}{c}
\text{Isomer 1} \\
\text{Isomer 2} \\
\text{Isomer 3}
\end{array} \] | unknown |
| $n=3$ | \[ \begin{array}{c}
\text{Isomer 1} \\
\text{Isomer 2} \\
\text{Isomer 3}
\end{array} \] | \[
\text{Structure 1} \\
\text{Structure 2} \\
\text{Structure 3}
\] |
| $[\text{In}]_n$-Ph | $n=1$ | \[ \begin{array}{c}
\text{Isomer 1} \\
\text{Isomer 2} \\
\text{Isomer 3}
\end{array} \] | \[
\text{Structure 1} \\
\text{Structure 2} \\
\text{Structure 3}
\] |
| $n=2$ | \[ \begin{array}{c}
\text{Isomer 1} \\
\text{Isomer 2} \\
\text{Isomer 3}
\end{array} \] | unknown |
| $n=3$ | \[ \begin{array}{c}
\text{Isomer 1} \\
\text{Isomer 2} \\
\text{Isomer 3}
\end{array} \] | \[
\text{Structure 1} \\
\text{Structure 2} \\
\text{Structure 3}
\] |
Reaction Proceedings of Polyurethane

FT-IR spectra of polyurethane are presented in Figure 8. Since every FT-IR spectrum does not show the typical N=C=O bands (located on 2270 cm\(^{-1}\)) \(^{41}\), isocyanate groups in polyisocyanate must react with hydroxyl groups in polyol and phenolic additives perfectly.

【Figure 8】 FT-IR spectra of every polyurethane.

Figure 8  FT-IR spectra of every polyurethane.
Properties of Polyurethane

Soaking Tests in Water

The weight change of polyurethane sheets soaked in water as a function of soaking time is presented in Figure 9. The weight of control (Ex.0) reached to a 2.7% of saturation at 14 days and the phenomenon could be caused by water absorption. The weight of the polyurethane sheets containing phenol (Ex.1) and \([St]_n\)-Ph (Ex.2) increased until 7 days and then changed into decrease, and after 32 days, became into a negative. While, the weight of the polyurethane sheet containing \([In]_n\)-Ph reached to a 1.5% of saturation at 21 days, and thereafter the weight did not change. Since the 1.5% of saturation was lower than the 2.7% of saturation on control, it was found that \([In]_n\)-Ph could be effective for decreasing water absorption on polyurethane and the effusion of \([In]_n\)-Ph into water would be lower than that of phenol and \([St]_n\)-Ph.

【Figure 9】 Relationship between change of weight and soaking time in water on the polyurethane containing the three phenolic additives: (□):Ex.0, (○):Ex.1, (△):Ex.2, (□):Ex.3

Figure 9  Relationship between change of weight and soaking time in water on the polyurethane containing the three phenolic additives: (□):Ex.0, (○):Ex.1, (△):Ex.2, (□):Ex.3
The concentration data of total organic carbon (TOC) in the water used for above soaking tests are presented in Table 2. TOC of the system with $[\text{In}]_n\text{-Ph}$ is much lower than that of control, and that with Ph and $[\text{St}]_n\text{-Ph}$ is much higher than that of control respectively. We considered that the phenomena would be caused by effusion of Ph and $[\text{St}]_n\text{-Ph}$ into water.

We described in our previous papers that a weak point of the phenolic additives is effusion into water$^{43,44}$. As shown in above results, we found that the weak point could be solved by using $[\text{In}]_n\text{-Ph}$ for a new phenolic additive.

Tensile Adhesion Strength as a Function of Salt-water Spraying Test (SST) time for an Index on Anticorrosion

Initial tensile adhesion strength of polyurethane anticorrosive coatings on steel plates and that treated with SST for 3000h are presented in Table 2. The deviations were within $\pm 5\%$, and in all cases interfacial destruction between polyurethane and adherents occurred.

Initial tensile adhesion strength of the systems with the phenolic additives was higher than that of control. We considered the reason that, i.e., since polyurethane without the phenolic additives is more rigid than that with them and the molecular mobility of polyurethane without the phenolic additives would not be able to follow the deformation rate, high adhesion strength could not be obtained. While, when the phenolic additives for plasticizers are contained in polyurethane, the adhesion strength would become higher because the molecular mobility of polyurethane could follow the deformation rate. But, when the polyurethane is too soft, high adhesion strength could not be obtained because the molecular cohesion of polyurethane would become low and then the destruction mode would change to a cohesive mode. So, when the phenolic additives plasticize polyurethane reasonably, tensile adhesion strength of polyurethane would be increased.$^{45}$

After SST, the tensile adhesion strength of polyurethane containing $[\text{In}]_n\text{-Ph}$ was higher than that of the others. So, it was found that $[\text{In}]_n\text{-Ph}$ is very effective for improving anticorrosion on polyurethane coatings.

Density

Density data of the polyurethane sheets are also presented in Table 2. The deviations were within $\pm 1\%$. It was found that density is increased by presence of the phenolic additives.

The increase of density can be explained in a term of “antiplastization”.$^{25-27}$ The concept of “antiplasticization” is that, i.e., the “antiplasticizer” of polar additives reduce the free volume that is available for molecular motion in stiff-chain of polymers. In a
term 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 equation 1\(^\text{46}\),

$$f = V_1 f_1 + V_2 f_2 + KV_1 V_2$$  \hspace{1cm} (1)

where, $K$ is an interaction parameter. For most polymer/additive systems, $K$ is generally negative but small ($\sim 10^{-2}$) 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 interaction parameter between the polymer and additive resulting is negative and large. Then the free volume is decreased with the additive and the modulus increases. From above term of “antiplastization”, we considered that the phenolic additives perform as “antiplasticizer” and then the densities of polyurethane with them increased.

Daly et al. reported a similar phenomenon on amine-cured epoxy resin systems, i.e., the density of cured epoxy was increased by an additive of the reaction product (EPPHAA) of 1,2-epoxy-3-phenoxypropane (EPP) and 4-hydroxyacetanilide (HAA).\(^\text{31}\)

**DMA**

DMA data are presented in Table 2, Figure 10 and Figure 11. As shown in Table 2, the storage modulus ($E'$) at $23 \degree C$ ($<T_g$) is decreased by the presence of the phenolic additives. It is a characteristic as plasticizers.

$E'$ data at $90 \degree C$ ($E'$ on rubbery plateau ) are also presented in Table 2. $E'$ of the polyurethane with $[\text{In}]_n$-Ph is lower than that with phenol or $[\text{St}]_n$-Ph. Generally, it is known that the cross-linking density ($\rho$) of cured resins is proportion to the $E'$ on rubbery plateau as shown in equation 2\(^\text{47}\).

$$\rho = \frac{E'}{3\phi RT}$$  \hspace{1cm} (2)

where, $\phi$ is Front Coefficient, usually, that is near equal to 1. $R$ is Gas Constant. $T$ is absolute temperature.

From the results, it was found that the cross-linking density of the system with $[\text{In}]_n$-Ph is much smaller than that of control. Whereas, the cross-linking density of the system with phenol or $[\text{St}]_n$-Ph is slightly smaller than that of control. The reason would be considered as follows. In the first place, since the reactivity between $[\text{In}]_n$-Ph and isocyanate would be higher than that between phenol or $[\text{St}]_n$-Ph and isocyanate, the urethane bond formed between phenol or $[\text{St}]_n$-Ph and isocyanate should be dissociated during a long period of curing, and then since isocyanate groups should be regenerated, urethane bonds between polyol and polyisocyanate should be reformed.

As shown in Table 2 and Figure 11, $T_g$ of the polyurethane containing phenol does not change in comparison with control. Whereas, $T_g$ of the polyurethane with $[\text{St}]_n$-Ph was much decreased. Furthermore, $T_g$ of the polyurethane with $[\text{In}]_n$-Ph was increased. It would be due to the rigid molecular structure of indene.
As shown in Figure 11, every tan\(\delta\) peak data of the polyurethane containing the phenolic additives is lower than that of control, especially, that with phenol is the lowest. It would be due to the fact that the motion of the matrix chains of polyurethane is restricted by the presence of the phenolic additives. Phenol showed the highest restriction.\(^4,7,19-21\)

【Figure 10】 Relationship between storage modulus (\(E'\)) and temperature on the polyurethane containing the three phenolic additives: (□);Ex.0, (○);Ex.1, (△);Ex.2, (□);Ex.3

Figure 10  Relationship between storage modulus (\(E'\)) and temperature on the polyurethane containing the three phenolic additives: (□);Ex.0, (○);Ex.1, (△);Ex.2, (□);Ex.3
【Figure 11】 Relationship between loss tangent (\(\tan \delta\)) and temperature on the polyurethane containing the three phenolic additives: ( □ ); Ex.0, ( △ ); Ex.1, ( ○ ); Ex.2, ( □ ); Ex.3

Figure 11  Relationship between loss tangent (\(\tan \delta\)) and temperature on the polyurethane containing the three phenolic additives: ( □ ); Ex.0, ( △ ); Ex.1, ( ○ ); Ex.2, ( □ ); Ex.3
TMA data of the polyurethane are presented in Figure 12 and the coefficients of thermal expansion ($\alpha_1$ and $\alpha_2$) given with TMA are also presented in Table 2. $\alpha_1$ is the coefficient of thermal expansion at the range of temperature between 10 $^\circ$C and 20 $^\circ$C (<Tg) and $\alpha_2$ is that at the range of temperature between 70 $^\circ$C and 80 $^\circ$C ( >Tg).

Every $\alpha_1$ of the systems with phenol and [In]$_n$-Ph is lower than that of control respectively, and $\alpha_2$ of the systems with phenol, [St]$_n$-Ph and [In]$_n$-Ph is also lower than that of control respectively. It might be caused by that, i.e., the free volume of the systems with phenol and [In]$_n$-Ph are decreased by the presence of phenol or [In]$_n$-Ph. Whereas, $\alpha_1$ of the system with [St]$_n$-Ph is higher than that of control. It might be due to that, i.e., Tg of the system with [St]$_n$-Ph is much lower than that of the others. So, at the much lower temperature range than that between 10 $^\circ$C and 20 $^\circ$C, $\alpha_1$ of the system with [St]$_n$-Ph should become the same as that of the systems with phenol and [In]$_n$-Ph.

Figure 12 TMA of the polyurethane containing the three phenolic additives.
**Tensile Strength and Elongation**

Tensile strength data and elongation data of the polyurethane are also presented in Table 2. The tensile strength of the polyurethane containing phenol is much higher than that of control, and that of the polyurethane containing [St]_n-Ph and [In]_n-Ph is a little lower than that of control respectively. While, every elongation of the polyurethane containing the three phenolic additives is higher than that of control. Only the deformation of the polyurethane containing phenol was ductile. It was reported that a ductile deformation is a character of “antiplasticizer”. As shown in Figure 11, the molecular motion of polyurethane containing phenol would be reduced because the tanδ peak is decreased. Hence, we considered that phenol performs as “antiplasticizer” rather than plasticizer. 7, 12

**CONCLUSIONS**

In order to find a new excellent phenolic additive for heavy duty anti-corrosive polyurethane coatings without coal tar, the polyurethane formulations with the three kinds of model phenolic additives, i.e., phenol, styrene adducts with phenol ([St]_n-Ph) and indene adducts with phenol ([In]_n-Ph), were prepared and investigated the properties. As the results, it was found that [In]_n-Ph is a new good phenolic additive for heavy-duty anticorrosive coatings of polyurethane as follows.

1. The weight decrease of the polyurethane coatings containing [In]_n-Ph during soaking tests in water was much lower than that of the polyurethane with phenol, [St]_n-Ph and that without the phenolic additives.

2. After SST, the tensile adhesion strength of the polyurethane coatings containing [In]_n-Ph was much higher than that with phenol, [St]_n-Ph and that without the phenolic additives, i.e., [In]_n-Ph showed a good anticorrosive properties.

3. Every density of the polyurethane containing the three phenolic additives was higher than that of control. The phenomena would be caused by a decrease in the free volume of polyurethane in the presence of the phenolic additives.

4. Since the density of polyurethane was increased by the presence of [In]_n-Ph, it was found that [In]_n-Ph also has a property for “antiplasticizer” property. But, because the E’ and the elongation was increased, as well as the tensile strength was increased, [In]_n-Ph should be regarded as plasticizer rather than “antiplasticizer”.
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