

Properties of Modified Polyurethane with Phenols Adducted with Aromatic Olefins

—New Applications of Polycyclic Aromatics Contained in Coal Tar—

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1. INTRODUCTION

For elastic adhesives of civil engineering and construction, for base films of dicing tapes of semiconductor chips and for protection coatings of Tape Automated Bonding(TAB), a new type of elastic polyurethane have been required.^{1), 2)} In addition, we have a mission to develop new applications of polycyclic aromatic compounds contained in coal-tar produced by Nippon Steel Chemical Co., Ltd. Against the background of above requirements, we have been developing polyurethane modified with phenols adducted with aromatic olefins.³⁾ We synthesized modified polyurethane with phenols adducted with aromatic olefins of styrene, indene and vinyl-naphthalene and then we measured a relationship between tensile strength and elongation, a relationship between lap-shear adhesion strength and T-peel adhesion strength, a relationship between viscoelasticity and temperature and a change of weight as a function of time during dipping in water. In this paper, we reported the results and presented the characteristics of the modified polyurethane.

2. EXPERIMENTAL

2.1. Synthesis of Phenols Adducted with Aromatic Olefins

Phenol, p-toluene-sulfonic-acid(PTS) for an initiator and toluene for a solvent were put into a 200ml flask. Over 1h, 50% toluene solutions of 3 kinds of aromatic olefins were added to a 200ml flask by syringe. An addition rate of PTS was 2wt% on a basis of total amount of an aromatic olefin and phenol. Over 1h, a reaction presented in Figure 1 was performed at 85°C. Calcium hydroxide was added and PTS was neutralized. The neutralization reaction was performed at 85°C for 15 minutes. A neutralization product and extra calcium hydroxide were filtered off, and evaporation was carried out in vacuo at 200°C, and then 3 kinds of phenols adducted with aromatic olefins, i.e., phenol adducted with styrene([St]_n-Ph), phenol adducted with indene([In]_n-Ph) and phenol adducted with vinyl-naphthalene([VN]_n-Ph), were obtained.

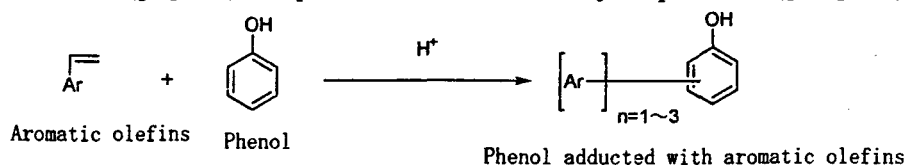
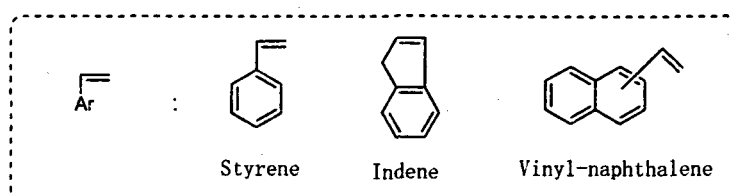


Figure1 Synthesis of phenol adducted with aromatic olefins



2.2. Synthesis of Modified Polyisocyanate with Phenols Adducted with Aromatic Olefins

Phenols adducted with aromatic olefins, polyisocyanate and a solvent were put into a 200ml flask. For polyisocyanate, polymeric-MDI(Coronate1130 produced by Nippon Polyurethane Industry Co., Ltd., Japan) with 135.1g/eq of equivalent weight of isocyanate groups was used. For a solvent, a mixture of toluene(50phr), MIBK(30phr) and MEK(20phr) was used. Over 1h, a reaction presented in Figure2 was performed at 85°C.

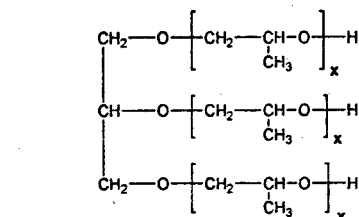
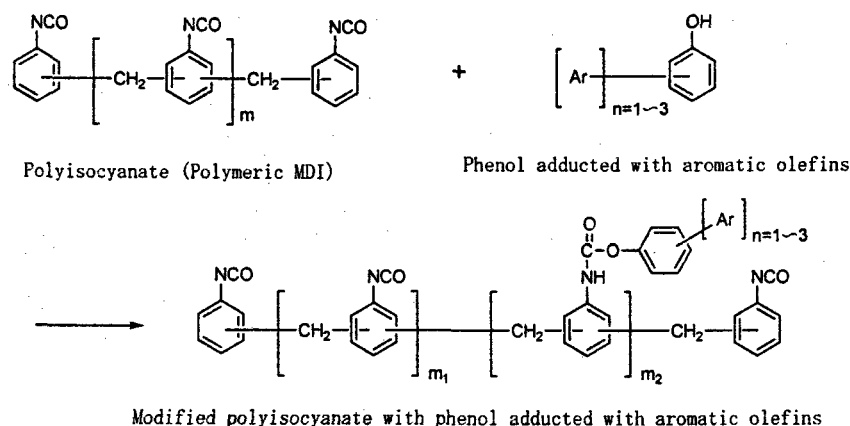


Figure3 Chemical structure of polyol

Figure2 Synthesis of modified polyisocyanate with phenols adducted with aromatic olefins

2.3. Synthesis of Modified Polyurethane with Phenols Adducted with Aromatic Olefins

In accordance with Table1, polyol, modified polyisocyanate with phenols adducted with aromatic olefins and a solvent were put into 300ml disposable cups and mixed. For polyol, polyetherpolyol(G-300 produced by Asahidenka Kogyo Co., Ltd., Japan) with 109.6g/eq of equivalent weight of hydroxyl groups was used. The chemical structure is presented in Figure3. Total weight of them was 200g. The mixtures were run into trays made from polypropylene. The mixtures were dried and cured for 21days at 23°C-65%RH and polyurethane sheets for test peaces were prepared.

Table1 Recipe of modified polyurethane with phenols adducted with aromatic olefins

Components	Ex. 0	Ex. 1	Ex. 2	Ex. 3	Ex. 4
Polyol	22.4	18.1	16.7	16.6	16.1
Polyisocyanate	27.6	0	0	0	0
Modified polyisocyanate with Ph (50% solution)	0	63.7	0	0	0
Modified polyisocyanate with [St] _n -Ph (50% solution)	0	0	66.6	0	0
Modified polyisocyanate with [In] _n -Ph (50% solution)	0	0	0	66.9	0
Modified polyisocyanate with [VN] _n -Ph (50% solution)	0	0	0	0	67.8
Solvent (Toluene:MIBK:MEK = 50:30:20 [phr])	50.0	18.1	16.7	16.5	16.1
Total	100	100	100	100	100
Ratio of NCO/OH	1.0	1.0	1.0	1.0	1.0

2.4. Measurements

(1) GPC

GPCs of phenols adducted with aromatic olefins were measured by using a GPC machine produced by Waters Co., Ltd., USA. For a solvent, THF was used.

(2) Equivalent Weight of Hydroxyl Groups

An equivalent weight of hydroxyl groups of phenols adducted with aromatic olefins was measured in accordance with JIS K 0070.

(3) Elongation and Tensile Strength

Cured polyurethane sheets for test pieces were cut to a dumbbell form of Type1 described in JIS K 6251 by using a cutting machine produced by Dumbbell Co., Ltd., Japan. Test pieces were set to a tensile tester (Autograph AGS-500 produced by Shimadzu Co., Ltd., Japan), and tensile strength and elongation were measured at 23°C-65%RH and at crosshead speed of 1mm/min.

(4) T-Peel Adhesion Strength

T-peel adhesion strength was measured in accordance with JIS K 6854. Stainless steel plates of SUS304 were used as adherents. Resin varnishes compounded in accordance with Table3 were coated on adherents with an area of 25mm×100mm and dried for 15 minutes at 23°C-65%RH. 2 sheets of the above coated adherents were mounted together through 2 stainless steel wires with 0.1mm in diameter for spacers and cured for 60days at 23°C-65%RH.

Test pieces were held to a chuck of a tension test machine (Autograph AGS-500 produced by Shimadzu Co., Ltd., Japan) and pulled by an upper chuck at crosshead speed of 5mm/min and at 23°C-65%RH. Measurements were done 4 times and the averages were adopted as T-peel tensile adhesion strength.

(5) Lap-Shear Adhesion Strength

Lap-shear adhesion strength was measured in accordance with JIS K 6850. Stainless steel plates of SUS304 were also used as adherents. Resin varnishes compounded in accordance with Table3 were coated on adherents with an area of 12.5mm×25mm and dried for 15 minutes at 23°C-65%RH. 2 sheets of the coated adherents were also mounted together through 2 stainless steel wires with 0.1mm in diameter for spacers and cured for 60days at 23°C-65%RH.

Test pieces were held to a chuck of a tension test machine (Autograph AGS-500 produced by Shimadzu Co., Ltd., Japan) and pulled by an upper chuck at crosshead speed of 1mm/min and at 23°C-65%RH. Measurements were done 4 times and the averages were adopted as lap-shear tensile adhesion strength.

(6) Dynamic Viscoelasticity

Cured sheets described in 2.3. were cut to a size of 5×30mm and used as test pieces. DMS 6100 produced by SEIKO Instrument Co., Ltd., Japan, was used as a dynamic viscoelastometer. Frequency was 10Hz. Temperature was raised from 20°C to 200°C. Heating rate was 2°C/min.

(7) Weight Changes of Polyurethane Sheets as a Function of Time during Soaking in Water

Polyurethane sheets described in 2.3. were cut to a size of 50mm×50mm and used as test

pieces. Test pieces were put into 300ml disposable cups with filling pure water and measured changes of weight as a function of time for 46days at 23°C-65%RH.

(8) Soxhlet Extracts of Polyurethane Sheets with Ion-Exchange Water and Measurement of Total Organic Carbon(TOC) in the Extracted Water

For pre-treatments, soxhlet extracts of polyurethane sheets with ion-exchange water were performed. Soxhlet extracts were performed over 8h at boiling point of water. A measurement machine for TOC was used TOC-500 produced by Shimadzu Co., Ltd. Japan.

3. RESULTS AND DISCUSSION

3.1. Properties of Phenols Adducted with Aromatic Olefins

Properties of phenols adducted with aromatic olefins are presented in Table2. Compositions of adduct were calculated by an area percent of GPC peaks. Molecular weight of GPC peaks was determined with standard polystyrene samples. For example, a GPC of phenol adducted with indene is presented in Figure4.

Table2 Properties of phenols adducted with aromatic olefins

Phenols adducted with aromatic olefins	Composition of adduct [GPC area%]					Equivalent weight of hydroxyl groups [g/eq]
	n=0	n=1	n=2	n=3	Others	
[St] _n -Ph	4.9	47.1	39.2	8.4	0.4	241
[In] _n -Ph	6.7	49.1	37.4	6.7	0.2	267
[VN] _n -Ph	3.7	44.4	33.7	12.2	6.0	291

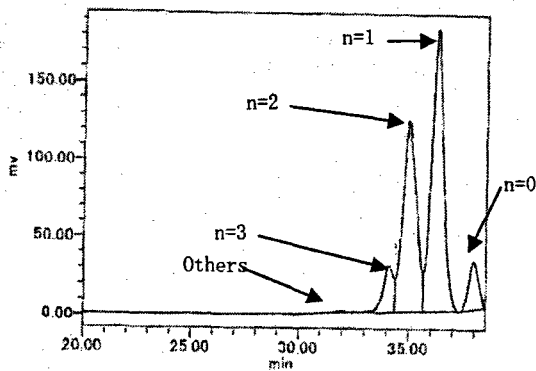


Figure4 GPC of phenol adducted with indene

3.2. Properties of Modified Polyurethane with Phenols Adducted with Aromatic Olefins

3.2.1. Tensile Strength and Elongation

Effects of modification on relationships between tensile strength and elongation on polyurethane are presented in Figure5. We found that elongation of polyurethane modified with [In]_n-Ph(Ex.3) and that of polyurethane modified with [VN]_n-Ph(Ex.4) increased with a little decrease of tensile strength on a basis of control(Ex.0). On the other hand, we found that elongation of polyurethane modified with Ph(Ex.1) and polyurethane modified with

[St]_n-Ph(Ex.2) did not increase on a basis of control(Ex.0).

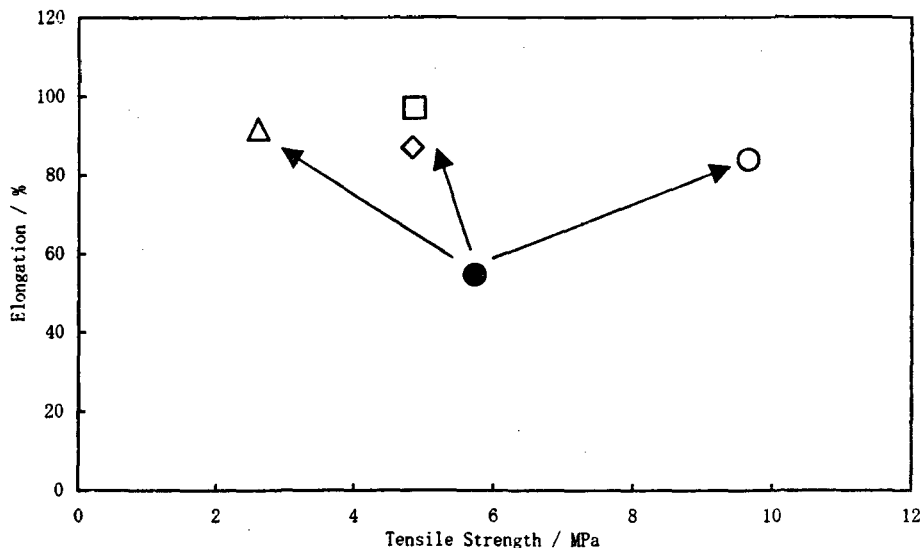


Figure 5 Effect of modification on relationship between elongation and tensile strength of polyurethane. : (●);Ex. 0, (○);Ex. 1, (△)Ex. 2, (□)Ex. 3, (◇)Ex. 4

3.2.2. Lap-Shear Adhesion Strength and T-Peel Adhesion Strength

Effects of modification on relationships between lap-shear adhesion strength and T-peel adhesion strength are presented in Figure 6. We found that T-peel adhesion strength of polyurethane modified with [In]_n-Ph(Ex.3) and that of polyurethane modified with [VN]_n-Ph(Ex.4) increased with a little decrease of lap-shear adhesion strength on a basis of control(Ex.0). On the other hand, we found that lap-shear adhesion strength of polyurethane modified with Ph(Ex.1) increased but the T-peel adhesion strength did not increase. Furthermore, we found that lap-shear adhesion strength of polyurethane modified with [St]_n-Ph(Ex.2) decreased and T-peel adhesion strength of Ex.2 did not increase.

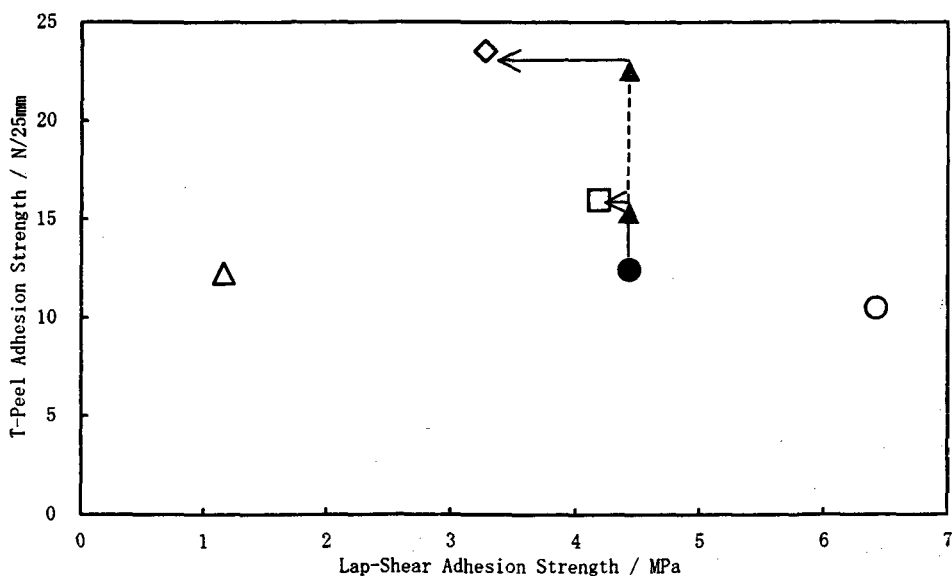


Figure 6 Effect of modification between T-peel adhesion strength and lap-shear adhesion strength on polyurethane : (●);Ex. 0, (○);Ex. 1, (△)Ex. 2, (□)Ex. 3, (◇)Ex. 4

3.2.3. Dynamic Viscoelasticity

Effects of modification on relationships between storage modulus and temperature are presented in Figure 7. We found that both curves of polyurethane modified with $[In]_n$ -Ph(Ex.3) and polyurethane modified with $[VN]_n$ -Ph(Ex.4) shifted to a high temperature side on a basis of control(Ex.0), i.e., we found that both Tg of Ex.3 and Ex.4 increased together. On the other hand, we found that both curves of polyurethane modified with Ph(Ex.1) and polyurethane modified with $[St]_n$ -Ph(Ex.2) shifted to a low temperature side on a basis of control(Ex.0), i.e., we found that both Tg of Ex.1 and Ex.2 decreased together.

At a temperature region of rubber-like state, storage modulus of Ex.1 and Ex.2 were the same as that of Ex.0, i.e., cross-linking densities of Ex.1 and Ex.2 did not decrease. We speculated that the reason was due to that during a keeping period of curing, urethane bonds, which were formed between phenolic hydroxyl groups in modifiers and isocyanate groups in polyisocyanate, were reduced and isocyanate groups were reclaimed, as the results, a cross-linking reactions were restarted on Ex.1 and Ex.2. On the other hand, storage modulus of Ex.3 and Ex.4 at a temperature region of rubber-like state were lower than that of Ex.0, i.e., we found that cross-linking densities of Ex.3 and Ex.4 did not decrease. We speculated that the reason was due to that during a keeping period for curing, urethane bonds, which were also formed between phenolic hydroxyl groups of modifiers and isocyanate groups, did not be reduced and then cross-linking reactions did not be restarted on Ex.3 and Ex.4.

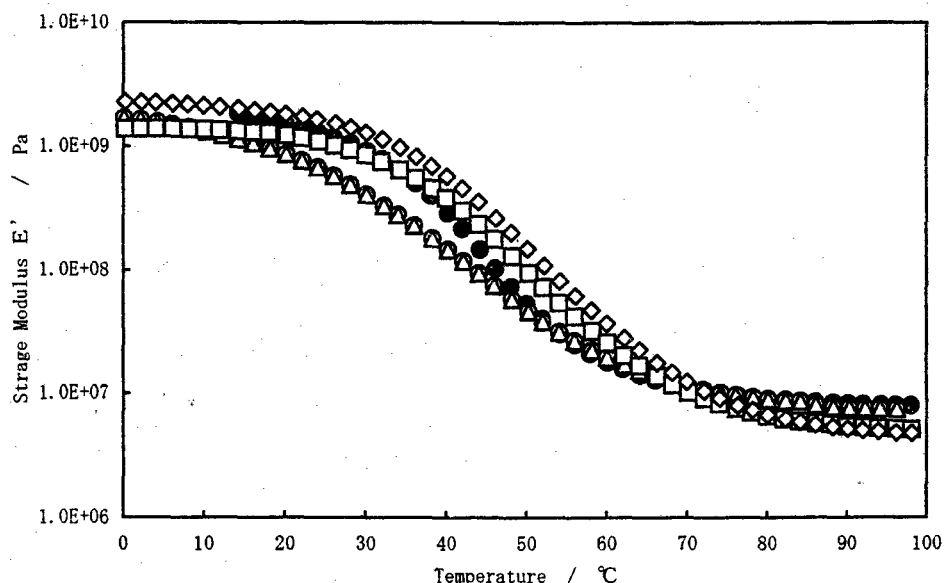


Figure 7 Effect of modification between storage modulus and temperature on polyurethane :
(●);Ex.0, (○);Ex.1, (△);Ex.2, (□);Ex.3, (◇)Ex.4

Effects of modification on relationships between $\tan \delta$ and temperature are presented in Figure 8. Similarly, we found that both curves of polyurethane modified with $[In]_n$ -Ph(Ex.3) and polyurethane modified with $[VN]_n$ -Ph(Ex.4) shifted to a high temperature side on a basis of control(Ex.0). We also found that both Tg of Ex.3 and Ex.4 increased together. When polyurethane was modified with phenol adducted with aromatic olefins, a cross-linking density of polyurethane decreased. In spite of them, Tg of polyurethane modified with $[In]_n$ -Ph(Ex.3) and polyurethane modified with $[VN]_n$ -Ph(Ex.4) increased. We speculated that the reason was due to rigid molecular structures of indene and vinyl-naphthalene.

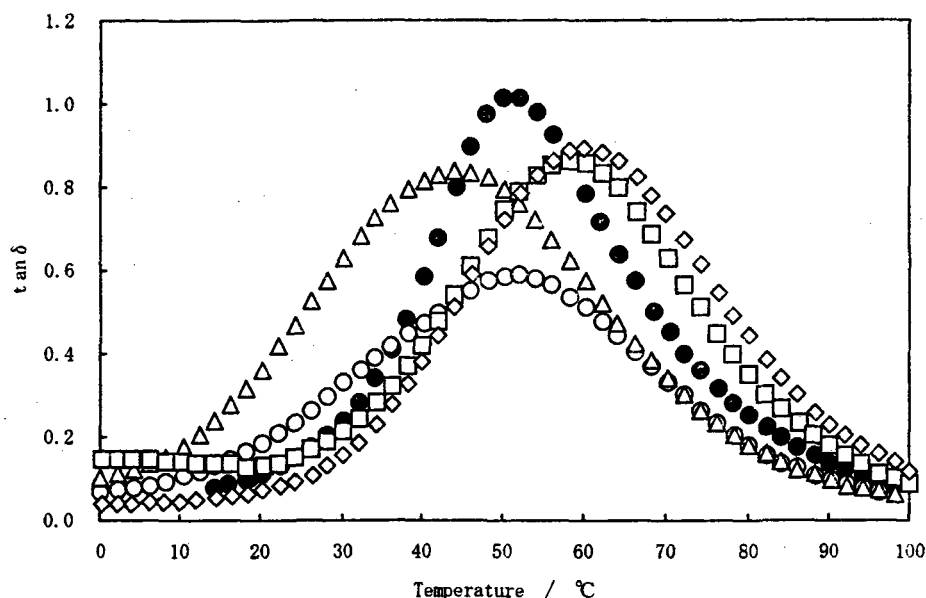


Figure 8 Effect of modification between $\tan \delta$ and temperature on polyurethane: (●);Ex. 0, (○);Ex. 1, (△);Ex. 2, (□);Ex. 3, (◇);Ex. 4

3.2.4. Weight Changes of Polyurethane Sheets as a Function of Time during Soaking in Water

Weight changes of polyurethane sheets as a function of time during soaking in water are presented in Figure 9. On control (Ex. 0), we found that increase of weight, which may be due to water absorption, saturated with 2.7% at 14 days. On polyurethane modified with Ph (Ex. 1) and polyurethane modified with $[St]_n$ -Ph (Ex. 2), we found that until 7 days the weight increased, and after 7 days the weight changed into decrease. Furthermore, on Ex. 1 and Ex. 2, we found that after 32 days an increase rate of weight changed into a negative. We speculated that the phenomena were caused by that, i.e., Ph and $[St]_n$ -Ph run into water. On the other hand, on polyurethane modified with $[In]_n$ -Ph (Ex. 3) and polyurethane modified with $[VN]_n$ -Ph (Ex. 4), we found that both increase rates of weight saturated with 1.5% at 21 days together. Since 1.5% of Ex. 3 and Ex. 4 was lower than 2.7% of control (Ex. 0), we found that modifications with $[In]_n$ -Ph (Ex. 3) and $[VN]_n$ -Ph (Ex. 4) were effective to improve an absorbent property of polyurethane.

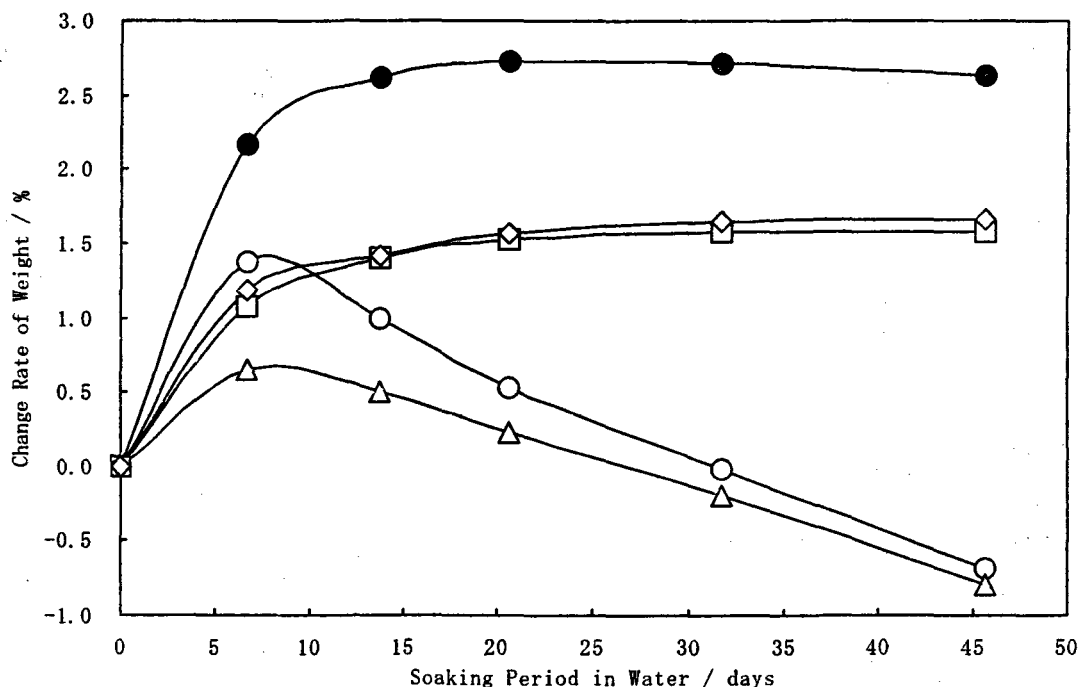


Figure 9 Effect of modification between change rate of weight and soaking period in water on polyurethane: (●);Ex. 0, (○);Ex. 1, (△);Ex. 2, (□);Ex. 3, (◇);Ex. 4

3.2.5. Soxhlet-Extract of Polyurethane Sheets with Ion-Exchange Water and Concentration of Total Organic Carbon(TOC) in the Extracted Water

Measurement results of total organic carbon(TOC) in ion-exchange water, in which polyurethane sheets were soxhlet-extracted, are presented in Table3. TOC of Ex.3 was much lower than that of Ex.0 and TOC of Ex.4 was also lower than that of Ex.0. On the other hand, TOC of Ex.1 was much higher than that of Ex.0 and TOC of Ex.2 was also higher than that of Ex.0.

Already, we speculated the reason why at a rubber-like temperature region, storage modulus of Ex.1 and Ex.2 were the same as that of Ex.0 and storage modulus of Ex.3 and Ex.4 were lower than that of Ex.0 was due to that, i.e., urethane bonds of Ex.1 and Ex.2 were reduced and urethane bonds of Ex.3 and Ex.4 did not be reduced. Regarding the results of Figure9, we speculated that Ph(Ex.1) and [St]_n-Ph(Ex.2) run into water much more than [In]_n-Ph(Ex.3) and [VN]_n-Ph(Ex.4). We considered that the above speculations could be supported by the results presented in Table3.

Table3 TOC (Total Organic Carbon) in soxhlay-extracted polyurethane with water

	Ex. 0	Ex. 1	Ex. 2	Ex. 3	Ex. 4
TOC [m g / L]	98.6	957	154	68.3	84.1

4. CONCLUSION

Modified polyurethane with phenols adducted with styrene, indene and vinyl-naphthalene of aromatic olefins, which were contained in coal-tar or derived from components contained in coal-tar, were synthesized and measured the properties. On modified polyurethane with phenols adducted with indene and vinyl-naphthalene, we found characteristics below.

- (1) Elongation increased with a little decrease of tensile strength.
- (2) T-peel adhesion strength increased with a little decrease of lap-shear adhesion strength.
- (3) Tg increased.
- (4) Absorption rate of water decreased.

From the above characteristics, we would like to apply our modified polyurethane to elastic adhesives of civil engineering and construction, base films of dicing tapes for semiconductor chips and protection coatings for TAB.

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