Improved Heat and Solvent Resistance of a Pressure-Sensitive Adhesive Thermally Processable by Isocyanate Dimer Dissociation

Kazutaka Asada,[1,2] Kenji Fukano,[1] Keiji Yamashita,[2] Eiji Nakanishi[2]

[1]Central Laboratory, Nichiban Co., Ltd, 3-1-10 Nihongi-shinmachi, Anjo City, Aichi Prefecture 446-0075, Japan
[2]Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya City, Aichi Prefecture 466-8555, Japan
Correspondence to: K. Asada (E-mail: k-asada@nichiban.co.jp)

ABSTRACT: Methods that do not involve use of an organic solvent are being considered for manufacturing environmental-friendly pressure-sensitive adhesive tapes. Among these methods, the hot-melt method exhibits high productivity but is somewhat limited in terms of performance. Hot-melt-fabricated pressure-sensitive adhesives require heating fluidization and cooling solidification, and it is extremely difficult to improve their heat resistance. We examine thermally processable pressure-sensitive adhesives with a completely new structure, fabricated based on the thermal dissociation of the isocyanate dimer. This enables thermal processing of materials softened by thermal dissociation. Fabrication of crosslinkable pressure-sensitive adhesive becomes possible through a reaction of isocyanate caused by dissociation of its dimer. It is found that improving thermal and solvent resistances, which are disadvantages associated with conventional hot-melt pressure-sensitive adhesives, is potentially possible with the pressure-sensitive adhesive reported here. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41444.

INTRODUCTION

Benefits of pressure-sensitive adhesives include: (1) adhesion immediately after application; (2) accurate control of film thickness for thin sizes; (3) removability. Pressure-sensitive adhesives are therefore used in a broad range of applications, such as packaging tapes, double-sided tapes, labels, binding tapes, as well as pressure-sensitive adhesive plasters, tapes, and patches for medical applications. Most pressure-sensitive adhesives in the past were solvent types based on natural rubber. At present, however, they are fabricated using acrylics, synthetic rubbers, silicones, urethanes, and various other types of polymers. Research into manufacturing methods that do not involve the use of solvents has been conducted in recent years as a response to environmental concerns. Consequently, aqueous-emulsion pressure-sensitive adhesives, hot-melt pressure-sensitive adhesives, and ultraviolet (UV)-curable pressure-sensitive adhesives have been developed and implemented. Hot-melt pressure-sensitive adhesives in particular present cost advantages with production aspects such as high coating speeds and compact facilities; these lead to high production volumes, especially for packing tapes.[1]

Mainstream hot-melt pressure-sensitive adhesives use styrene-based triblock copolymers as thermoplastic elastomers. Styrene-based triblock copolymers have styrene blocks on both ends, connected by an ABA-type triblock structure of covalently bonded block units with low T_g and low compatibility with styrene. Films formed from styrene-based triblock copolymers are separated at the microphase level into domains of styrene blocks and of intermediate blocks.[2] Such films show rubber elasticity through prevention of fluidization with the pseudo-crosslinking structure of a glassy styrene block, coupled with flow due to the melt of the styrene domain when heated. This has made it possible to impart processability owing to the thermoplasticity of rubber when heated, significantly contributing to the realization and development of hot-melt pressure-sensitive adhesives. Practical implementations of acrylic triblock copolymers with superior weather resistance and transparency have been achieved recently; studies of applications for hot-melt pressure-sensitive adhesives are in progress.[3] Technologies for manufacturing pressure-sensitive adhesive tapes comprising base material and pressure-sensitive adhesive, such as those in which the film and pressure-sensitive adhesive layers are formed simultaneously with a multilayer extruder, have also been developed.[4]

It is difficult to improve their thermal resistance, because this system required heating fluidization and cooling solidification phenomenon. Such copolymers tend to have lower molecular
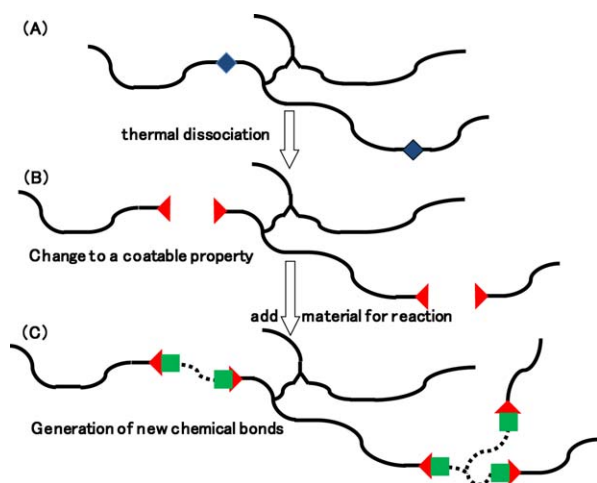
Figure 1. Schematic diagram of new thermal processing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

weights than the natural rubber or acrylic polymers used as pressure-sensitive adhesives, due to the balance that must be sustained with melting viscosity. In order for them to function as a pressure-sensitive adhesive, it is also necessary to include a tackifier resin, which is oligomeric in nature, to the block copolymer. Hot-melt pressure-sensitive adhesives, therefore, have poor solvent resistance. There are also potential problems due to residues of low-molecular-weight components and contamination.

Various trials which improve the heat and solvent resistance of a hot-melt pressure-sensitive adhesive have been performed. Although there have been trials using a styrene-based triblock copolymer system, where crosslinking in the multi-functional monomer is induced by energy sources such as an electron beam (EB) or UV, this is not the technology generally used.[5,6] Hot-melt acrylic systems have also been developed in recent years, using acrylic polymers functionalized with photo-reactive groups; after being applied when hot, these systems are exposed to UV or an EB. Some of these systems have been commercialized.[7–9] However, problems with cost, facilities load, and productivity exist with these techniques; therefore it is adapted to only a limited set of uses.

To resolve the shortcomings of pressure-sensitive adhesives of the conventional hot-melt type, we investigated thermally processable adhesives of a completely new type that are not dependent on thermoplasitcity. As a method of adding processability (fluidization) by heating, we attempted to employ dissociation of chemical bonds. We also used the generation of new chemical bonding between the dissociated parts to increase the cohesive strength after processing.

A schematic of the thermal process for pressure-sensitive adhesive which we investigated is shown in Figure 1. Dissociation of thermally dissociable parts in the base material results in molecular chains being cut, adding processability (fluidization) to the material: (A) → (B). If an active group can be thermally dissociated, then a new bonding mechanism becomes possible. We

examined the results of adding chemical compounds with functional groups that can react with dissociated components, generating different polymers after the thermal process: (B) → (C). Any type of thermally-dissociable components can be used so long as the dissociation results in generation of active groups.

In our investigation, the isocyanate dimer (uretdione ring) was used. The uretdione ring has a four-member ring structure created by the reaction of isocyanate in the presence of a catalyst, such as alkylphosphine, arylalkylphosphine, pyridine, or trimethylamine; this uretdione ring is known to reproduce isocyanate when heated. For example, the 2,4-toluene diisocyanate dimer has been reported to dissociate at 150°C.[10] It has also been reported to form an allophanate or biuret structure at lower temperatures, under conditions where alcohol and amine coexist.[11,12] Uretdione is used industrially as a hardening agent, adhesive conditioner, and crosslinker. In recent years, uretdione has been used as a hardener in blocking agent-free powder coatings. Much research has been done on manipulating the physical properties of these coatings, as well as their required process temperature (resolution temperature).[13–16]

Thermally processable hot-melt pressure-sensitive adhesives made using styrene triblock copolymers are processed at 150–200°C, and hence are compatible with the thermal dissociation temperature of isocyanate dimer. As they react easily with compounds that contain active hydrogen, such as hydroxyls, uretdione rings can be easily employed for the synthesis of polymers by using diisocyanate dimer. The uretdione rings were selected as the thermal dissociation part due to such properties as ease of synthesis and ease of implementation into materials, and the thermal dissociation condition is identical to the present processing temperature for hot-melt pressure-sensitive adhesives.

When an uretdione ring thermally dissociates, isocyanate with high reactivity is generated. It is therefore possible to generate new bonds by adding a polyol to the material that has been thermally fluidized. Molecular weights and the crosslinking structure can also be controlled, depending on the types of compounds added. As tackifier resins or oils are not included as essential components, there is a potential for resolving the shortcomings of conventional hot-melt pressure-sensitive adhesives. Solvents are used in the polymerization of commercially available block polymers, but our method can potentially make the process completely free of solvents, which offers an advantage in reducing the environmental burden.

The pressure-sensitive adhesives reported here are classified as urethane-based pressure-sensitive adhesives. Nakamura[17] and others reported on crosslinking of the urethane pressure-sensitive adhesive and its physical characteristics. In addition, trials to improve its adhesive strength[18] and to apply it as a medical adhesive[19] are reported, however these reports do not include pressure-sensitive adhesives of the no- solvent hot-melt type. A urethane thermoplastic elastomer and urethane hot-melt adhesives exist in the thing in which a heat process is possible with a no-solvent by a urethane system. They have a thermoplastic domain, and since the cohesive property at the room temperature at the site is very strong, they have no tack. As

Table I. Materials Used in this Study

Product name	Molecular weight	The number of functional group	NCO %	OH-value	Remarks
Addlink® TT	348.3	2	24.1		TDI dimer
CORONATE® T-100	174.2	2	48.2		TDI
KURARAY POLYOL P10010	10000[a]	2		11.2	MPD/AA
KURARAY POLYOL P6010	6000[a]	2		19	MPD/AA
KURARAY POLYOL P2010	2000[a]	2		56	MPD/AA
KURARAY POLYOL F3010	3000[a]	3		56	MPD/AA/TMP
KURARAY POLYOL F510	500[a]	3		336	MPD/AA/TMP

TDI: 2,4-toluene diisocyanate, MPD: 3-methyl-1,5-pentanediol, AA: adipic acid, TMP: trimethylol propane.
[a] Number average molecular weight.

suitable tackifier resin does not exist like styrene-based thermoplastic elastomer, either, it is very difficult to make a pressure-sensitive adhesive from such materials.

Verification of the reaction of uretdione rings was performed for this report by first using a low-molecular-weight model compound, with 2,4-toluene diisocyanate as the isocyanate dimer. Polyester polyol was then used to fabricate polyurethane, and the behavior and performance of the pressure-sensitive adhesive was verified.

EXPERIMENTAL

Raw Materials

The dimer 2,4-toluene diisocyanate made by RheinChemie (product name: Addolink® TT) was used as our isocyanate dimer and 2,4-toluene diisocyanate made by Nippon Polyurethane Industry (product name: Coronate® T-100) was used as is, without purification. Polyester polyol synthesized from 3-methyl-1,5-pentanediol and adipic acid (manufactured by Kuraray) were used as polyols. A polyester polyol containing a trimethylolpropane structure was used for crosslinking. These materials were commercially available and used without purification. The raw materials used are shown in Table I, while their structures are shown in Figure 2. Using a PET # 25 as a backing film when creating a pressure-sensitive adhesive sheet. It is a film of polyethylene terephthalate (product name: LUMI-

RROR®) made by Toray Industries. Other raw materials were reagent grade products available on the market and used as is.

Synthesis of Model Compound

We mixed 2.03 g (5.8 mmol) of 2,4-toluene diisocyanate dimer with 21.5 g (290 mmol) of 2-methylpropyl alcohol, the alcohol being in excess in relation to the amount of isocyanate used (NCO : OH = 1 : 25), and agitated it for 4 weeks at 60°C to allow reaction. After verifying by infrared spectroscopy (IR) that the absorption by isocyanate had become negligible the product was cleansed with ethanol and vacuum dried. Similarly, 5.23 g (30 mmol) of 2,4-toluene diisocyanate (monomer) was mixed with 111.2 g (1500 mmol) of 2-methylpropyl alcohol, which was an excess in relation to the amount of isocyanate (NCO : OH = 1 : 25) and agitated for 1 week at room temperature. After verifying with IR that the absorption of isocyanate had diminished, the product was cleansed with ethanol and then vacuum dried. The structure of the product was verified using IR and ^{1}H-NMR measurements after cleansing and drying.

Synthesis of Polyurethane

To prepare samples, polyols as specified in Table I were mixed with 2,4-toluene diisocyanate dimer and also with 2,4-toluene diisocyanate monomer as needed to reach the ratio of NCO : OH = 1 : 1. An ARV-310 vacuum mixer manufactured by Thinky was used at low pressure to agitate the mixture, which was then thermally cured at 60°C for 1 week.
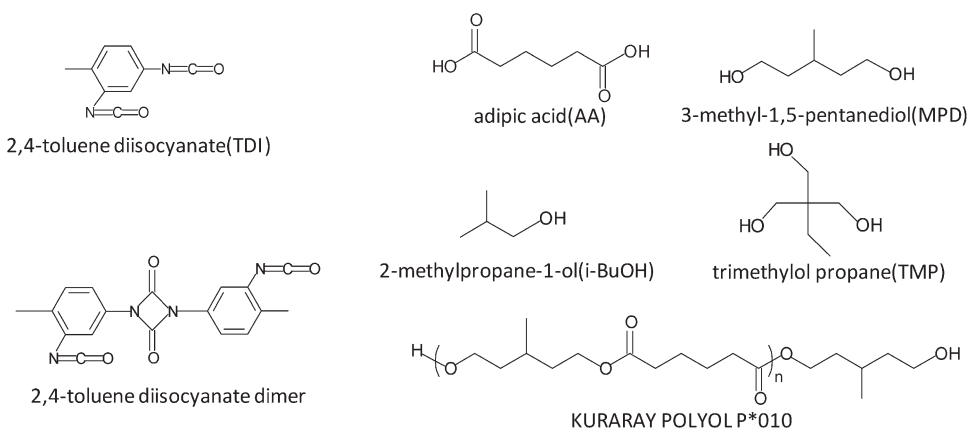

Figure 2. Structure of Materials used in this study.

Table II. Polyurethane Composition Used in this Study

Sample name	poly-ol for polyurethane (ur-ol)	TDI dimer (%)	TDI (%)	poly-ol for additives (ad-ol)
100P6	P6010	100	0	
75P6	P6010	75	25	No add (before heat process)
50P6	P6010	50	50	
25P6	P6010	25	75	
0P6	P6010	0	100	
50P6F30-1.0	P6010	50	50	F3010 100%,
50P6F30-0.3	P6010	50	50	F3010 30%, P2010 70%,
50P6F5-1.0	P6010	50	50	F510 100%,
100P6F30-0.3	P6010	100	0	F3010 30%, P2010 70%,
100P10F30-1.0	P10010	100	0	F3010 100%

%: Calculated from functional group equivalent.
###P&&F**-++ : ### shows the ratio of TDI dimer to TDI , && shows Mn^*10^{-3} of ur-ol , ** shows Mn^*10^{-2} of ad-ol , and ++ shows the ratio of F3010 [or F510] to P2010.

Dissociation Reaction of Model Compound
The model compound was poured into an ampule tube together with 2-methylpropyl alcohol, which was in excess in relation to the isocyanate generated by the dissociation of uretdione (1 : 200). After de-aerating and sealing the tube, the mixture was thermally processed for a prescribed amount of time in an oil bath at a prescribed temperature. The tube was then opened, and 2-methylpropyl alcohol that had not reacted was removed by distillation at low pressure.

Fabrication Method for Pressure-Sensitive Adhesive Sheets
Polyurethane with uretdione rings was heated and agitated in a Laboplast mill and R60 mixer manufactured by Toyo Seiki. Once softening of the material became evident, polyol was added and heat-mixed. A sheet was formed by heat pressing the mixture between release-coated papers. A base material of PET#25 was used as a laminate to prepare the pressure-sensitive adhesive sheet which was matured at 40°C for 5 days. The mixtures examined are shown in Table II.

Measurements
A Spectrum One FT-IR spectrometer manufactured by Perkin Elmer was used with a Universal ATR Sampling Accessory for IR measurements. An AN400N magnetic resonance spectrometer manufactured by Bruker was used for 1H-NMR measurements using DMSO-d6 as a solvent. Dynamic viscosity was measured with an MCR-301 rheometer manufactured by Anton Paar. The thermal distribution was measured using a 20-mm diameter parallel plate from −80 to 200°C, at a programmed rate of 5°C/min, a delay of 0.05% oscillation angle, and a frequency of 1 Hz. Melting viscosity was measured on a 20-mm diameter cone plate. Thermogravimetric analysis (TGA) was conducted using TGA-51, manufactured by Shimadzu Corporation, at a programmed rate of 5°C/min.

The peel adhesion was measured using a stainless-steel plate (SUS304) polished with abrasive paper and prepared as a test plate in accordance with the JIS Z 09237 (2000) standard. The test specimen was cut into 12-mm widths and attached to the plate by pressing with a 2-kg rubber roller. After 30 min, samples were peeled off at a rate of 300 mm/min using an RTM-100 manufactured by Orientec to measure the force values during peeling. An NS Probe Tack Tester manufactured by Nichiban was used to take measurement of probe tack values for 1 s retention time, using a 19.6-g mass at a head speed of 1 cm/min. The holding power was measured using a glass plate as a test surface in compliance with JIS Z 0237 (2000) with an attachment area of 12×20 mm^2 under a 500-g load, by measuring the amount of shifting that had occurred 1 h later. In cases where specimens dropped within 1 h, the drop time was measured.

RESULTS AND DISCUSSION

Verification of Reaction by Model Compound
The reactivity and pyrolytic properties of 2,4-toluene diisocyanate dimer have already been reported.[10–12] Since for our purpose the following three reactions must be applied, the reaction pathway shown in Figure 3 was used to perform reactions and to verify the structure under each condition. The three reactions are: the reaction that converts isocyanate on both ends to urethane while retaining the uretdione rings, that is, (I) → (II); the reaction that thermally dissociates the uretdione rings, that is, (II) → (III); the reaction that converts isocyanate generated from dissociation to urethane, that is, (III) → (IV). First, 2,4-toluene diisocyanate dimer (I) was reacted with 2-methylpropyl alcohol to convert the isocyanate on both ends to urethane. From the IR measurements, the absorption by urethane bonds appeared, and the absorption by isocyanate disappeared, which confirming that a urethane reaction had occurred. The fact that absorption by C═O of uretdione rings near 1780 cm^{-1} exists can be confirmed in both the before- and after-reaction spectra, while the fact that urethane bonding is generated in a condition where there are hardly any side reactions of the uretdione rings, such as dissociation or allophanate conversion, is also confirmed by the 1H-NMR results depicted in Figure 4. Next, (II) was heated to temperatures of 120–200°C in a nitrogen atmosphere to verify the occurrence of isocyanate due to dissociation of uretdione rings. The IR measurement results after heating are shown in Figure 5. The absorption near 2270 cm^{-1} by isocyanate is noted for heating at temperatures of 140°C and higher. There was a tendency for the absorption by isocyanate to increase as temperature increased, but the absorption arising from uretdione rings was not eliminated even when heated to 180°C for 6 h. This can be explained as follows: since the dissociation of uretdione rings is an equilibrium reaction, a portion of it was reconstituted during cooling between heating and the IR measurement.[11] When the specimen was heated to 200°C, it resulted in a mass reduction due to evaporation from the specimen, and the absorption spectrum also changed dramatically. This is presumed to be due to thermal dissociation of the urethane bond. Thermal stability of the urethane bond (IV) was evaluated by TGA. The measurement results
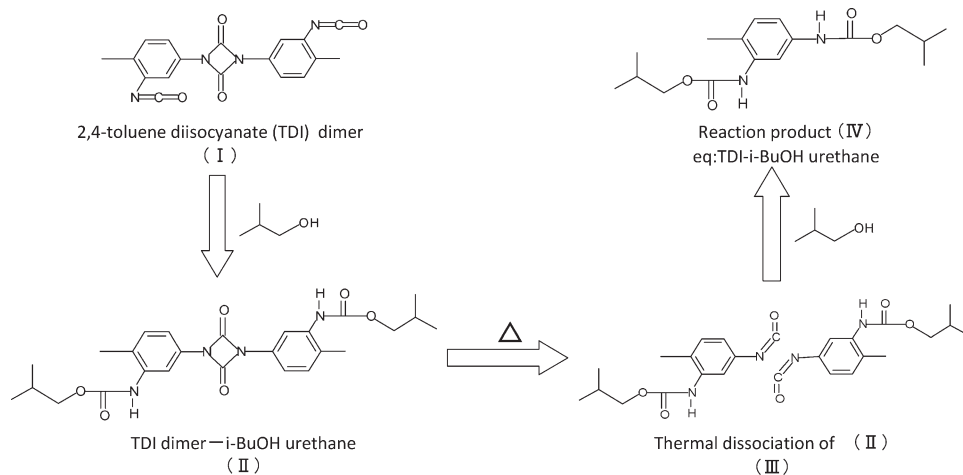
Figure 3. Reaction pathway.

are shown in Figure 6. The 0.1% mass reduction point was at 185°C, while the 1% point was at 217°C. It was determined from these results that the temperature range in which heat processing is possible without the destruction of the material due to thermal decomposition is 140–180°C. To verify that the isocyanate derived by thermal dissociation of uretdione rings reacted with compounds containing active hydrogen, (II) was heated in 2-methylpropyl alcohol. From the IR results , the C═O absorption of uretdione rings disappeared; as no absorption by isocyanate is seen, the isocyanate generated from the dissociation is believed to have reacted immediately with 2-methylpropyl alcohol. The product (IV) was confirmed to be identical to the compound obtained by reacting 2,4-tol-uene diisocyanate and 2-methylpropyl alcohol, based on the IR and ^{1}H-NMR measurements shown in Figure 7. Heating (II) causes dissociation of the uretdione ring, resulting in (III). Since the reaction from (II) to (III) is an equilibrium reaction, 2-methylpropyl alcohol exists in the system, and (III) reacts with 2-methylpropyl alcohol and changes into (IV). (III) has a structure of dissociated uretdione, and it has the same structure as the compound resulting from the equimolar reaction of 2,4-toluene diisocyanate, which is a monomer, with 2-methylpropyl alcohol. Since the fact that (IV) is the only product of the reaction according to IR and ^{1}H-NMR measurements, it is possible to judge that the reaction from (II) to (IV) progressed with hardly any side reactions.

Verification of Reactions with Polyurethane

An application to polymer materials was pursued as the following three aspects were confirmed in the previous section: (1) it is possible to generate urethane bonds by reacting iso-cyanate on both ends of 2,4-toluene diisocyanate dimer while retaining uretdione rings; (2) it is possible to thermally dissociate uretdione rings without decomposing urethane bonds by heating the urethane compound generated to a temperature of 140–180°C; (3) isocyanate generated by the dissociation reacts with coexisting hydroxyls to become urethane.

Polyurethane was synthesized at a ratio of NCO : OH = 1 : 1 by reacting polyester polyol synthesized by 3-methyl-1,5-
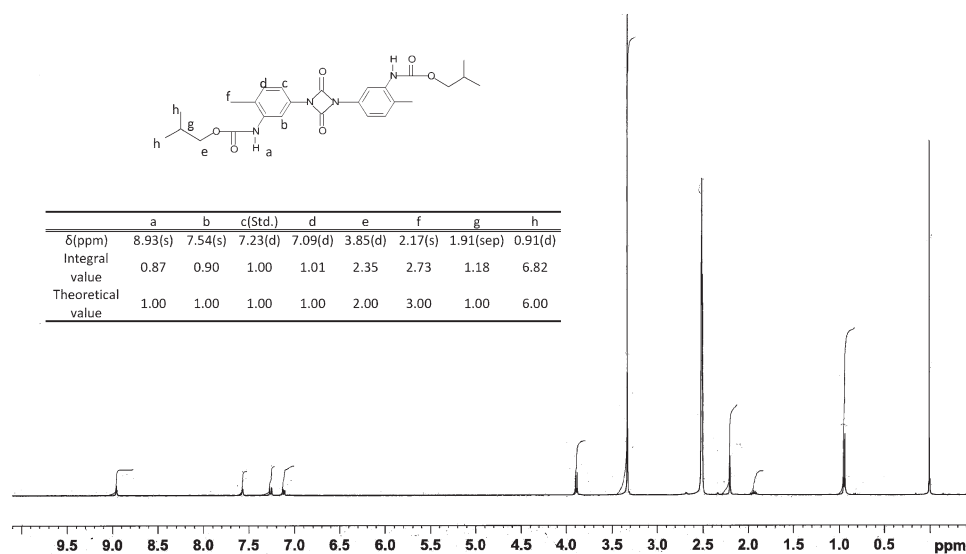

	a	b	c(Std.)	d	e	f	g	h
δ(ppm)	8.93(s)	7.54(s)	7.23(d)	7.09(d)	3.85(d)	2.17(s)	1.91(sep)	0.91(d)
Integral value	0.87	0.90	1.00	1.01	2.35	2.73	1.18	6.82
Theoretical value	1.00	1.00	1.00	1.00	2.00	3.00	1.00	6.00

Figure 4. ^{1}H-NMR Spectrum of TDI dimer–i-BuOH urethane (II).
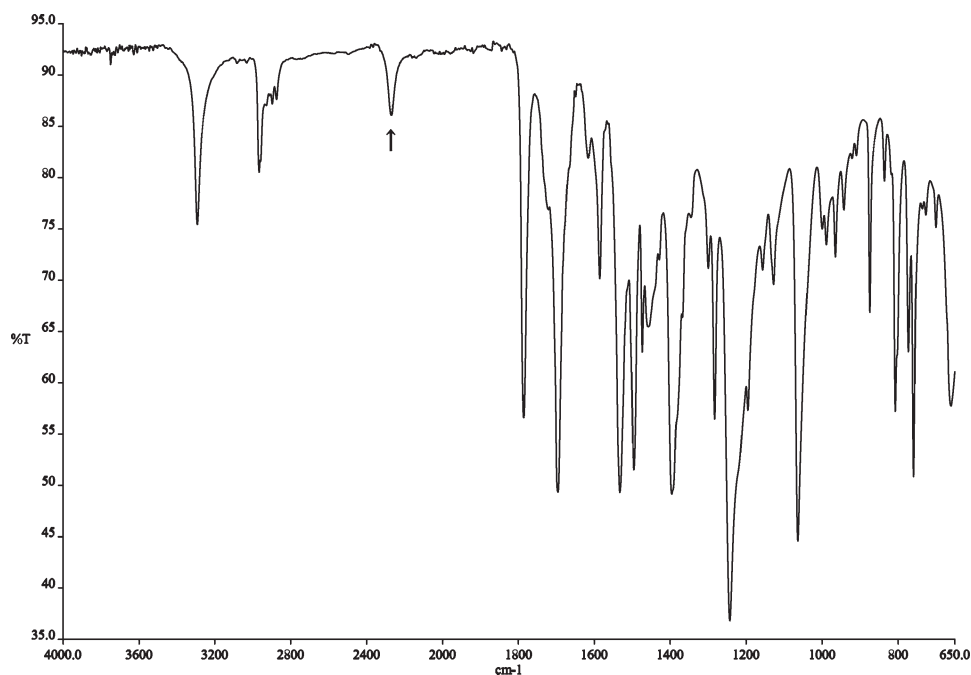
Figure 5. IR Spectrum of TDI dimer–i-BuOH urethane (II) after heat at 180°C for 6 h.

pentanediol and adipic acid with 2,4-toluene diisocyanate dimer as the pre-thermal process material. The IR spectrum of the polyurethane obtained is shown in Figure 8. Absorption was observed in the vicinity of 1780 cm^{-1}, confirming that this polymer had uretdione rings. The polymer obtained was heated to 160°C and agitated using a mixer; the change of the polymer to liquid was confirmed. The IR spectrum from liquefying polymers is shown in Figure 9. The disappearance of the absorption near 1780 cm^{-1} arising from uretdione rings was confirmed, as was the occurrence of absorption near 2270 cm^{-1} arising from isocyanate. Liquefaction of the polymer can therefore be determined from this result as being due to dissociation of the uretdione rings. This phenomenon does not create heating

fluidization such as the melting of cohesive domains in conventional hot melting would; the hypothesis that thermal processing becomes possible due to generation of fluidization through bond dissociation can be confirmed. Uretdione rings did not disappear even after heating for an extended time with compounds of lower molecular weights containing uretdione rings, but it had almost completely vanished after the polymers were hot mixed. As the density of uretdione rings is low in the case of polymers, and because the viscosity of the material is high, the probability of dissociated isocyanates re-forming bonds is low.

When synthesizing polyurethane, the ratio of NCO : NO = 1 : 1 was maintained, but two types of isocyanate, 2,4-toluene diisocyanate dimer and 2,4-toluene diisocyanate, were used to fabricate polyurethanes of various types by varying their proportions. Changes in the viscosity of the polyurethane when liquefied by hot mixing are shown in Figure 10. The melting viscosities of hot-melt pressure-sensitive adhesive using styrene triblock copolymer (SIS-HM) and the pressure-sensitive adhesive used for the coextrusion method are shown for comparison. The range of viscosity measured for the polyurethane was between that of ordinary hot-melt pressure-sensitive adhesives and coextrusion pressure-sensitive adhesives and was determined to be thermally processable using existing processing machines. The tendency of the viscosity to increase after fluidization was confirmed from the data for a low proportion of 2,4-toluene diisocyanate dimer; this is because the molecular weight of polymers after dissociation is higher and has a lower ratio of uretdione rings, which are components of the thermal dissociation. Such results indicate that it is possible to control viscosity to suit a processing machine by controlling the polymer structure.
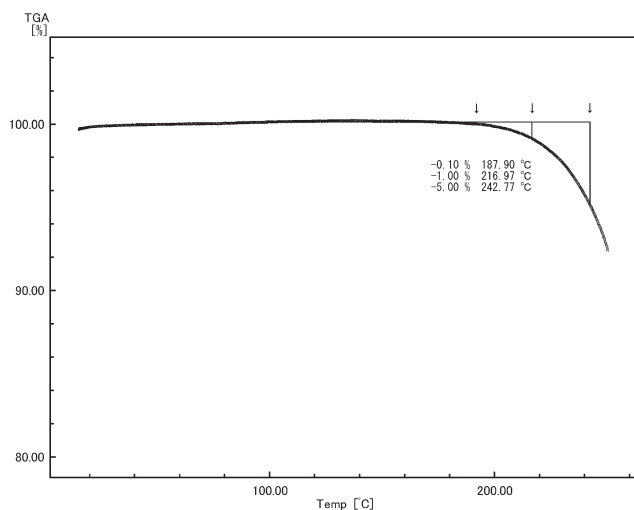

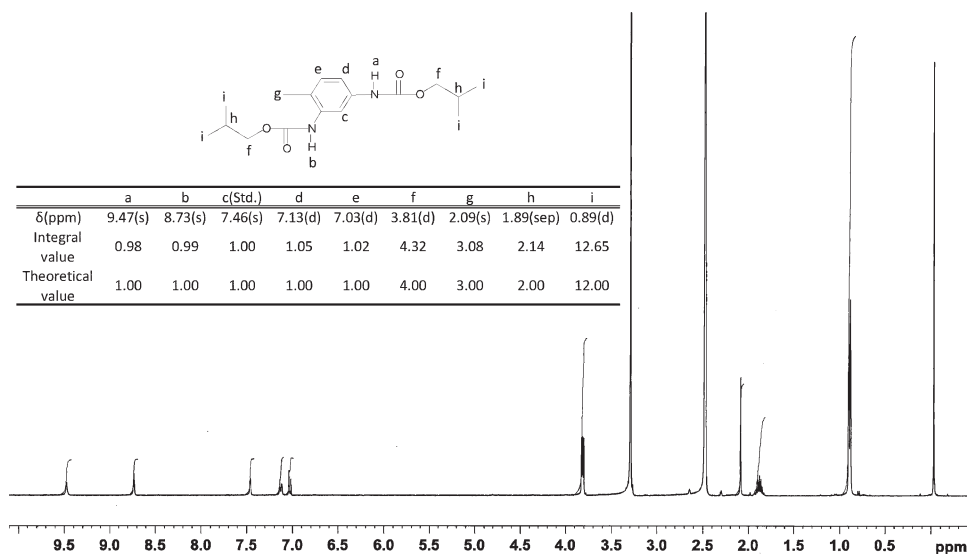**Figure 6.** TGA chart of TDI–i-BuOH urethane (IV).

Figure 7. ^{1}H-NMR Spectrum of the product obtained by heat treatment (II) in i-BuOH.

Compounds with functional groups that react with the isocyanate generated were added to the fluidized polymer and the mixture agitated. The compounds added in this instance were capped at the dissociated parts if they were mono-ols, while diols were inserted in the uretdione ring portion of the urethane bond, and the crosslinking structure is believed to be formed with triols or higher. A schematic diagram is shown in Figure 11. The effects on physical properties of the polymer after thermal processing were verified in our investigation by adding diols and triols. The mixture obtained from adding and agitating was sandwiched by release-coated papers and pressed in a heat press to form a sheet; then PET#25 was used as the base laminate material to prepare pressure-sensitive adhesive sheet samples. The IR spectra taken immediately after converting the compositions into sheets and after maturing them are shown in Figure 12(A,B), respectively. Absorption near 2270 cm^{-1} arising from isocyanate was observed immediately after conversion into sheets [Figure 12(A)], with the conversion into urethane by reactions with hydroxyls confirmed as not having reached its final point. In cases of lower molecular weight model compounds, conversion into urethane by the reaction progressed quickly after thermal dissociation, but the reactions with polymer materials were delayed. This is believed to have been due to the fact that in addition to a low functional group density, the viscosity of the material was high, resulting in a low collision frequency of functional groups.
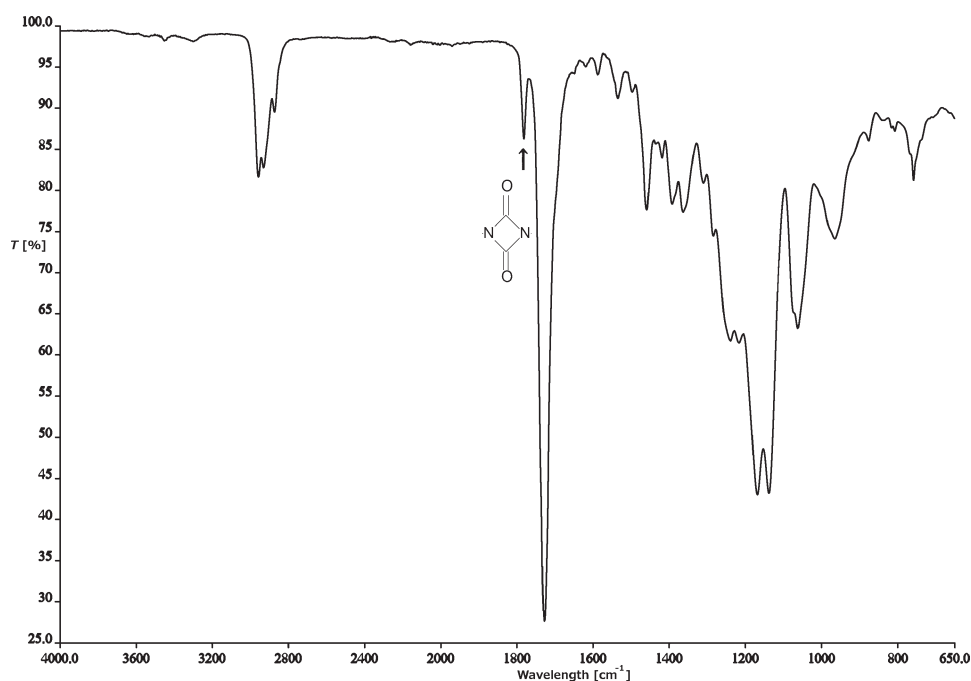

Figure 8. IR Spectrum of polyurethane (100P6) made from KURARAY POLYOL P6010 and addlink®TT.
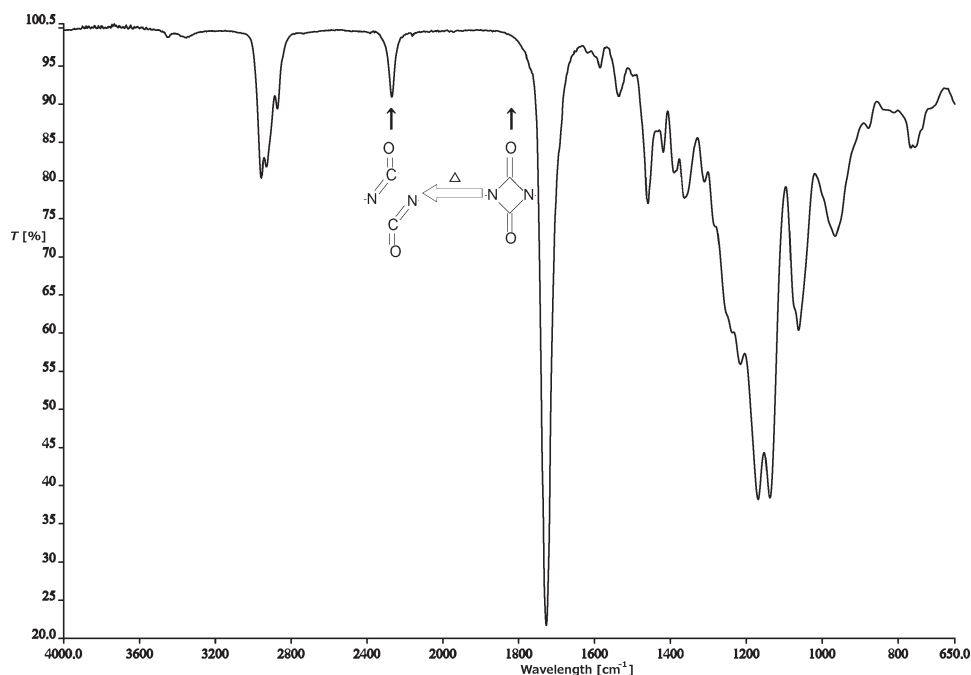
Figure 9. IR Spectrum of polyurethane (100P6) after heat at 160°C.

When the pressure-sensitive adhesive membrane is formed by a thermal process, the soft condition of the mixed material must be maintained until the material is formed into sheets. The fact that polymer materials react more slowly also indicates that it is possible to form them into sheets by heat processing. The absorption arising from isocyanate was confirmed to have disappeared after maturing [Figure 12(B). This shows that external irradiation such as UV or EB is not required to improve cohesive strength of the adhesive after coating, and shows that the energy costs, efficiency, and speedup of the coating process are superior in comparison to conventional crosslinked hot-melt pressure-sensitive adhesive.

Dynamic Viscosity Evaluation
Various polyurethanes were synthesized by changing the ratio of 2,4-toluene diisocyanate dimer to 2,4-toluene diisocyanate. The
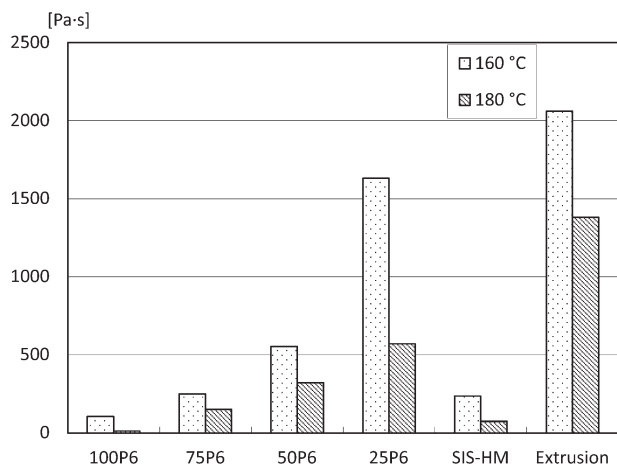
dynamic viscosity measurements for the polymer obtained are shown in Figure 13. The results indicate that there is a tendency for harder solids to result from higher dimer ratios, while softer material resulted from lower dimer ratios. This is likely because the structure of the dimer is a four-member ring planar structure with high cohesiveness and high restriction of molecular movement. This fact can be surmised from the fact that the solubility of 2,4-toluene diisocyanate dimer in a solvent is extremely low. The fact that the modulus decreases in proportion to the dimer ratio indicates that even materials with higher modulus and indicating no tack prior to thermal processing can have tack appearing as the modulus becomes lower; this is due to the loss of structures derived from the dimer after thermal processing. This shows that there may be advantages over conventional techniques due to the ease of handling raw materials at the time of adhesive tape production. Commercially available radiation-curable acrylic hot-melt pressure-sensitive adhesive has a high viscosity body of high tack before processing, but low cohesive strength, creating large handling difficulties. In contrast, the raw materials for pressure-sensitive adhesives produced by this technique have low tack, and we can expect that in both transportation and measurement during fabrication, they will be much easier to handle than conventional products.

Measurements of the dynamic modulus of a sample (50P6F3-1.0) obtained from adding polyester polyol with three functional groups, equivalent to the amount of isocyanate generated by dissociation, to a sample with a 50 : 50 ratio of 2,4-toluene diisocyanate dimer to 2,4-toluene diisocyanate, are shown in Figure 14. A reduction in the storage modulus (G') was observed in the sample when the thermal process was in the range from the glass transition point (-51°C) to near 60°C, in comparison with the sample before thermal processing. This is believed to be due to the loss of dimer structure. The results
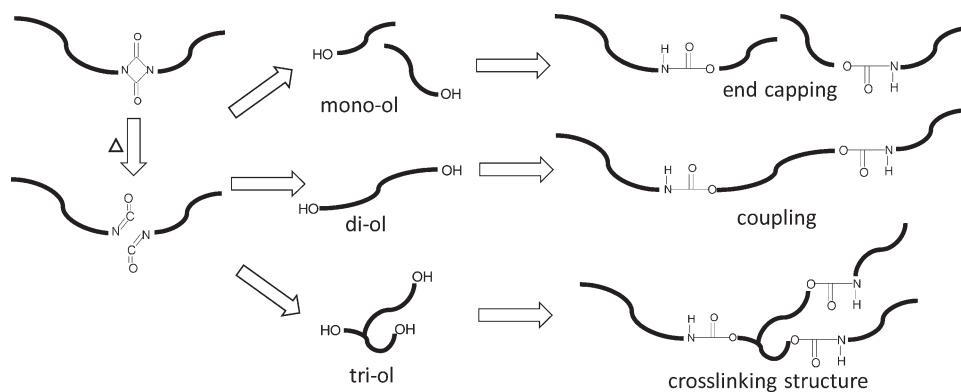

Figure 10. Viscosity of heated polyurethane.

Figure 11. Difference in reaction by various -ol.

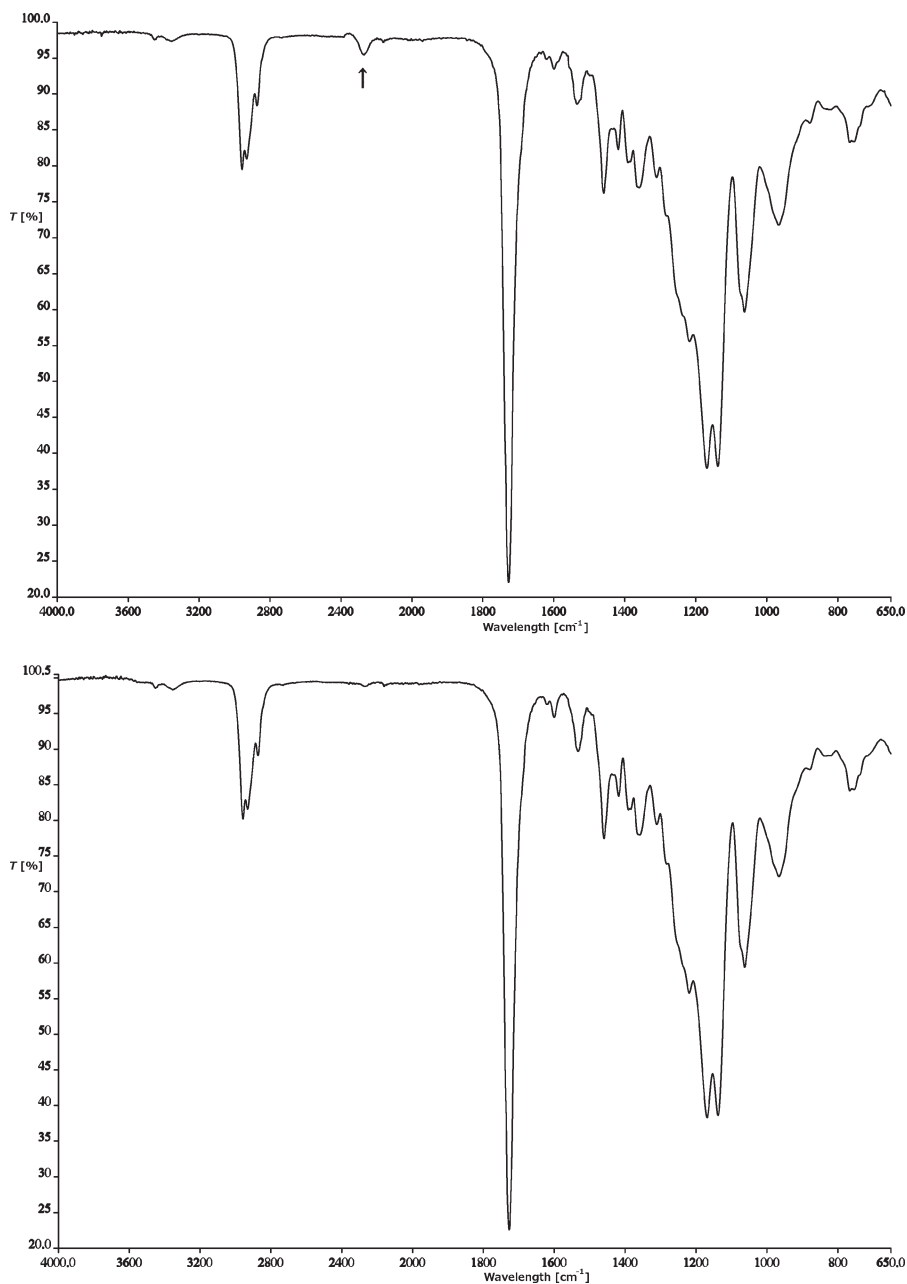**Figure 12.** (A) IR Spectrum of polyurethane (100P6F30-0.3) after hot press. (B) IR Spectrum of polyurethane (100P6F30-0.3) after aging.
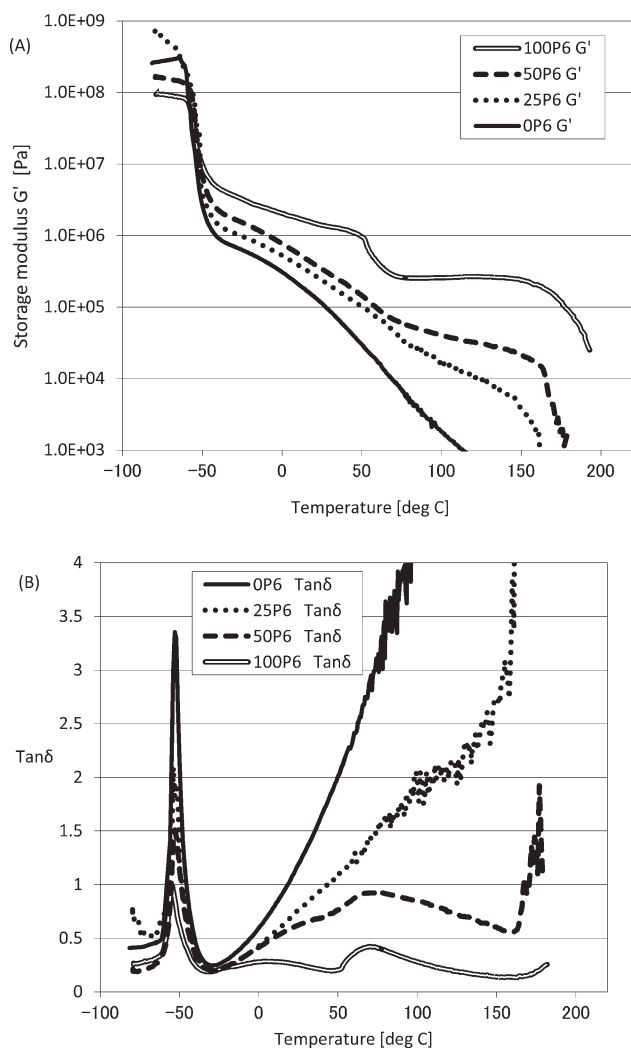
and the low-temperature G' is not affected. It is thought that crosslinking disturbs flow, and increased molecular motion at higher temperatures creates the change in G'. When there are many crosslinking points, the polymer movement at higher temperature is disturbed more and our data confirms that it becomes easy to fluidize if there are fewer crosslinks. The sample with the molecular weight of the added three-functional-group polyester polyol changed from 3,000 to 500 (50P6F5-1.0) indicating a result in which the storage modulus (G') of the rubbery condition (planar) region increased. If there is a short distance between crosslinking points, molecular chains crowd near a crosslinking point, and it is thought that the hardness of materials is increased because of polymer chain compaction. The sample with the molecular weight of polyol used for fabricating polyurethane before thermal processing changed from 6000 to 10,000 (100P10F30-1.0) indicated a decline in the storage modulus (G'). This is probably caused by increased mobility due to increase in the distance between urethane bonds that occurred as the number of urethane bonds, which indicates cohesiveness, decreased. These results indicate not only what kinds of structures should be selected for fabricating polyurethane before thermal processing
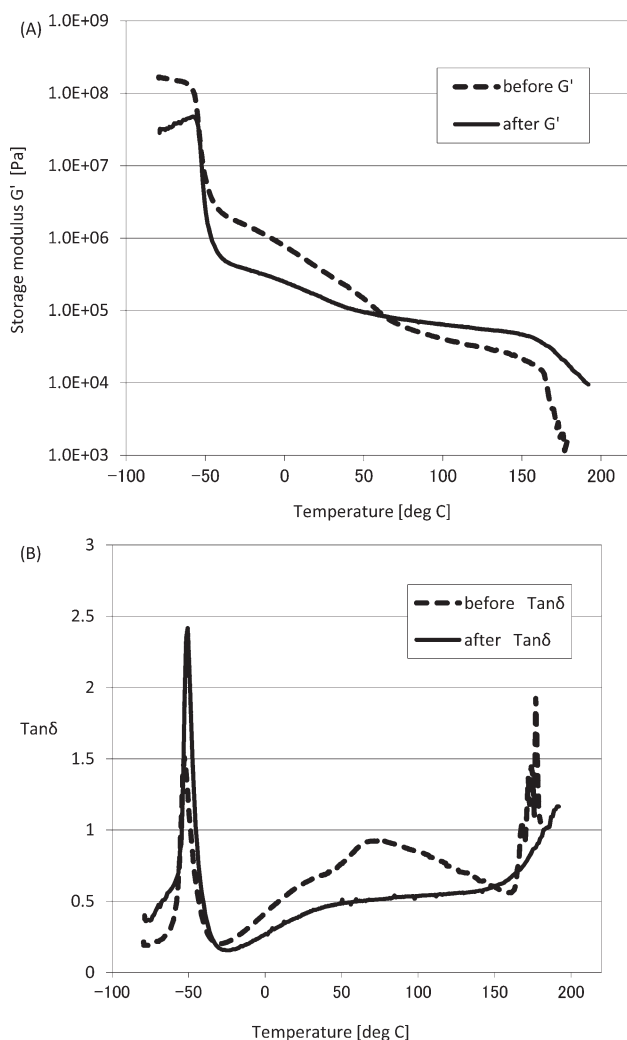

Figure 13. (A) Storage modulus (G') and (B) loss tangent (tan δ) plotted against temperature for **P6 before heat.

near 60°C and above, however, indicate higher G' in samples after the thermal process. This is probably because a crosslinking structure was formed after processing. Furthermore, the storage modulus (G') decreased rapidly beginning around 155°C, which is believed to be due to dissociation of the uretdione rings.

The influences of additive polyol (ad-ol) at thermal processing and the influences of the molecular weight of polyol (ur-ol) which used at synthesis of original polyurethane on their storage modulus (G') are shown in Figure 15. The results indicating a decline in storage modulus (G') were derived from ambient temperature to high temperature with samples (50P6F30-0.3) in which 70% of polyester polyol with three functional groups added to (50P6F30-1.0) was replaced by that with two functional groups. The polyester polyol with three functional groups contributes to the formation of the crosslinked structure as shown in Figure 11. Because a crosslinking point is formed in the section between dissociated parts, structures may have a long distance between crosslinking points. As a result of the increased distance, the restriction of molecular movement by crosslinks is reduced,

Figure 14. (A) Storage modulus (G') and (B) loss tangent (tan δ) plotted against temperature for 50P6F30-1.0 before and after heat treatment.
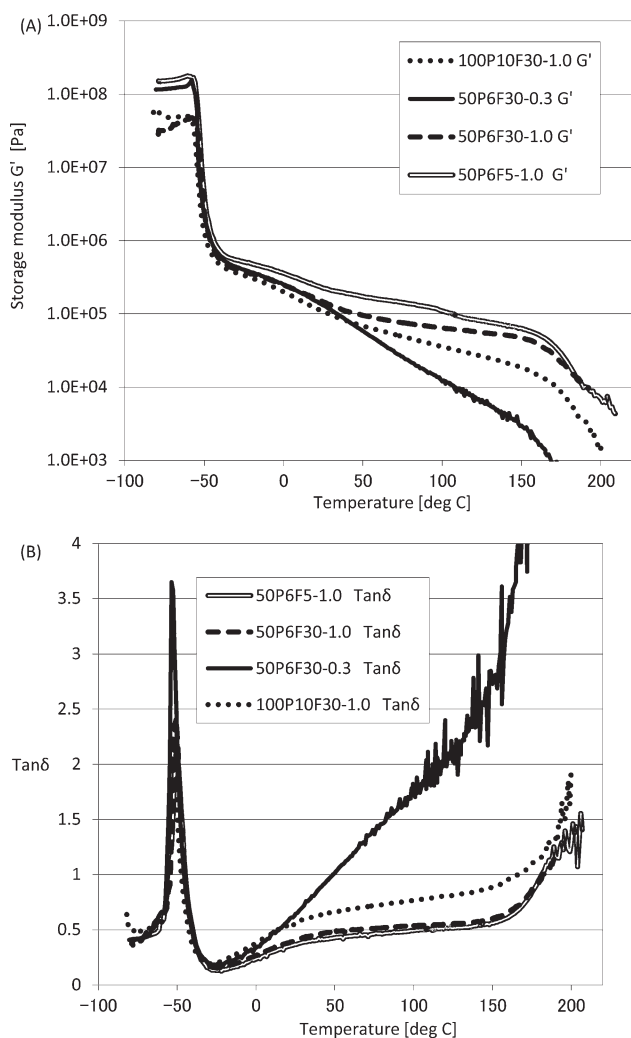
Figure 15. (A) Storage modulus (G') and (B) loss tangent (tan δ) plotted against temperature for **P**F** after heat treatment.

but also that the properties can be controlled by selecting the polyols that are added during thermal processing.

A comparison of the fabricated pressure-sensitive adhesive and a pressure-sensitive adhesive that uses styrene-block copolymer, which is a typical hot-melt pressure-sensitive adhesive (SIS/Tackifier/oil = 100/100/20), is shown in Figure 16. A rapid decline in the storage modulus (G') was observed with pressure-sensitive adhesives that use styrene-block copolymers at temperatures above ∼100°C. This is believed to be due to fusion of the styrene phase. The pressure-sensitive adhesive we fabricated, however, had the rubber condition region extending to near 160°C due to crosslinking, suggesting more favorable thermal resistance than conventional hot-melt pressure-sensitive adhesives. Furthermore, the pressure-sensitive adhesive using styrene-block copolymers reaches T_g at about −10°C and the rubbery condition (planar) region from around 5°C, but our new thermally processable pressure-sensitive adhesive reaches T_g near −50°C and rubber condition planar region near −35°C, suggesting that improvement in low-temperature performance over conventional products is possible as well.

Evaluation of Pressure-Sensitive Adhesive Properties

The pressure-sensitive adhesive properties of the film obtained through the thermal process are shown in Table III. The possibility of realizing pressure-sensitive adhesives with a good balance of the three fundamental properties of adhesion (peel adhesion), tack, and cohesive strength, is indicated. This suggests the potential for achieving thermally processable pressure-sensitive adhesives with a new bonding structure by thermal dissociation of bonds and chemical reaction using isocyanate dimers. The comparison of 50P6F30-1.0 and 50P6F30-0.3 which have different amounts of three-functional-group polyol, which become the crosslinking points, indicates that the retention power of 50P6F30-0.3 (with a lesser number of crosslinking structures), which showed cohesive failure in 27 min, was less than for 50P6F30-1.0, which exhibited shifting of 0.3 mm after 1 h. These two outcomes indicate an increase in cohesive strength with increased crosslinking; simultaneously, tack decreased to 2.95 N/5 mm diameter from 5.6 N/5 mm diameter This trend is similar to ordinary pressure-sensitive adhesives that use synthetic polymers.[20] This result indicates that even with identical polyurethane material prior to thermal
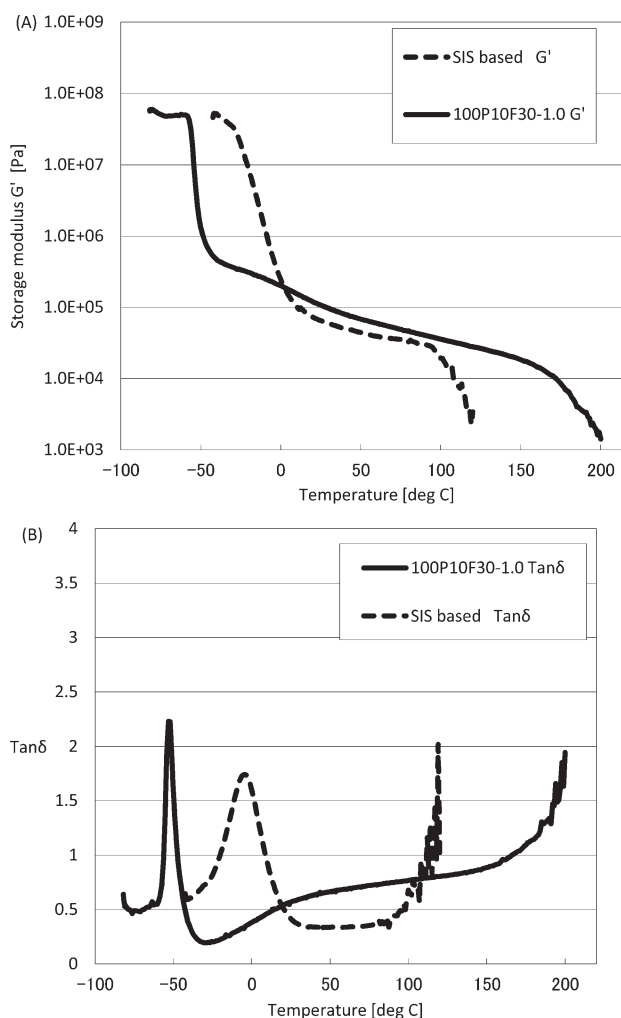

Figure 16. (A) Storage modulus (G') and (B) loss tangent (tan δ) plotted against temperature for 100P10F30-1.0 and SIS based adhesive.

Table III. Pressure-Sensitive Adhesive Properties

Sample name	poly-ol for polyurethane (ur-ol)	poly-ol for additives (ad-ol)	Peel adhesion to SUS [N/12 mm]	Probe tack [N/5 mmφ]	Holding power [mm/12 × 20 mm^2, 0.5 kg, 1 h]
50P6F30-1.0	P6010	F3010 100%	14.26 SS	2.95	0.3
50P6F30-0.3	P6010	F3010 30%. P2010 70%	2.18 CF	5.65CF	27 min. CF
50P6F5-1.0	P6010	F510 100%	6.47	2.48	0.2
100P10F30-1.0	P10010	F3010 100%	16.74 CF	4.85	1.6

SS, slip-stick and CF, cohesive failure.

processing, the pressure-sensitive adhesive properties can be controlled by the amounts and types of polyol (ad-ol) used during processing. The results for sample 50P6F5-1.0, with shorter distances between crosslinking points produced by reducing the molecular weight of the three-functional-group polyol, indicate an improvement in cohesive strength and deterioration of peel adhesion from 14.26 N/12 mm to 6.47 N/12 mm. A significant deformation of the pressure-sensitive adhesive occurred during peeling of 50P6F30-1.0 with a longer distance between crosslinking points, and it consumed a large amount of energy, whereas the amount of deformation can be verified as being small with 50P6F5-1.0. The increase of peel adhesion and decrease of cohesive strength were observed with 100P10F30-1.0, formulated with a higher molecular weight polyol for making polyurethane before processing. Such results match the pressure-sensitive adhesive properties expected from the greater reduction in the storage modulus (G') in the high-temperature regions as a result of fewer three-functional-group polyols. G' also decreases with greater molecular weights of polyols, as shown in Figure 15. The results obtained thus far suggest that the methods for controlling pressure-sensitive adhesive properties are follows. To increase peel adhesion or tack; (1) The number of crosslinking points should be decreased by decreasing amount of the additive polyols (ad-ol) having tri or higher OH groups. (2) The distance between the crosslinlking points should be increased by increasing the molecular weight of additive polyol (ad-ol). (3) The distance between the urethane bonds in polyurethane should be increase by increasing the molecular weight of polyol (ur-ol). To increase cohesive strength; In the synthesis of polyurethane or in the thermal processing, we should use a large number of polyols having much functional groups and lower molecular weight.

A verification of solvent resistance was performed by immersion in solvent, using 50P6F30-1.0, to confirm that a shortcoming of conventional thermally processable pressure-sensitive adhesives has been resolved as intended in this research. A pressure-sensitive adhesive disk with a diameter of 10 mm was immersed in toluene. The pressure-sensitive adhesive that used styrene-block copolymer dissolved completely within 1 h. However, while some swelling was confirmed with 50P6F30-1.0, the specimen held its shape after being immersed for 24 h. This is believed to have been due to the induction of the crosslinking structure during processing, in addition to not including additives of lower molecular weights in the pressure-sensitive adhe-sive. This result suggests that fabrication of pressure-sensitive adhesive products with solvent resistance, which had been a shortcoming for conventional pressure-sensitive adhesives, can be improved with pressure-sensitive adhesives thermally processed to produce new structures.

CONCLUSIONS

We examined thermally processable pressure-sensitive adhesives with a new structure developed using thermal dissociation of isocyanate dimer; these are potentially environmentally-friendly pressure-sensitive adhesives. Polyurethanes fabricated using isocyanate dimers can be made to have sufficient pressure-sensitive adhesive strength by processing with thermal dissociation of uretdione rings and can be changed into polymers with practical pressure-sensitive adhesive properties after processing by reacting with polyol. Such pressure-sensitive adhesives can be fabricated from the synthesis of polymers without solvents through the entire process; in comparison, commercial hot-melt pressure-sensitive adhesive needs a solvent for polymerization. There is also no need for additives of lower molecular weights, such as tackifier resins. It is also possible to control properties using polyol added during processing, and crosslinking structures can be implemented without outside energy sources such as UV or EB. Pressure-sensitive adhesives fabricated with the new structures have the potential to circumvent several disadvantages of conventional thermally processable pressure-sensitive adhesives, namely their heat and solvent resistance.

AUTHOR CONTRIBUTIONS

REFERENCES

1. Kenkichi, T. *Convertech* **2005**, *384*, 34.

2. McIntyre, D.; Campos-Lopez, E. *Macromolecules* **1970**, *3*, 322.

3. Fumi, A. *J. Adhes. Soc. Jpn.* **2013**, *49*, 336.

4. Katsunori, T.; Yasuyuki, I.; Hajime, N.; Hitoshu, T. The 49th Symposium on Adhesion: The Adhesion Society of Japan, **2011**, p 21.

5. Sakuma, N.; Suzuki, K. *Secchaku* **1985**, *29*, 272.

6. Park, Y. J.; Lim, D. H.; Kim, H. J.; Joo, H. S.; Do, H. S. *J. Adhes. Sci. Technol.* **2008**, *22*, 1401.

7. Cashion, M. P.; Park, T.; Long, T. E. *J. Adhes.* **2009**, *85*, 1.

8. Czech, Z. *Int. J. Adhes. Adhes.* **2004**, *24*, 119.

9. Czech, Z. *Coating* **2008**, *41*, 13.

10. Querat, E.; Tighzert, L.; Pascault, J. P.; Dušek, K. *Angew. Makromol. Chem.* **1996**, *242*, 1.

11. Singh, P.; Boivin, L. *Can. J. Chem.* **1962**, *40*, 935.

12. Arnold, R. G.; Nelson, J. A.; Verbanc, J. J. *Chem. Rev.* **1957**, *57*, 47.

13. Schmitt, F.; Wenning, A.; Weiss, J. V. *Prog. Org. Coatings* **1998**, *34*, 227.

14. Spyrou, E.; Metternich, H. J.; Franke, R. *Prog. Org. Coatings* **2003**, *48*, 201.

15. Smolka, M. G.; Lehmann, D.; Lehmann, F. *Polym. Prep.* **2003**, *44*, 58.

16. Morita, H.; Westhues, U. M. *Shikizai* **1998**, *71*, 637.

17. Nakamura, Y.; Nakano, S.; Ito, K.; Imamura, K.; Fujii, S.; Sasaki, M.; Urahama, Y. *J. Adhes. Sci. Technol.* **2013**, *27*, 263.

18. Shigemori, K.; Ochi, K. *J. Adhes. Soc. Jpn.* **2002**, *38*, 364.

19. Shikinami, Y.; Morita, S.; Tsuta, K.; Taniguchi, M. *Kobunshi Ronbunshu* **1992**, *49*, 19.

20. Satas, D. In Handbook of Pressure Sensitive Adhesive Technology, 3rd ed.; Satas, D., Ed.; Satas & Associates: Warwick, Rhode Island, **1999**; Chapter 10, p 171.