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Themoreversible Cross-Linking Rubber Using Supramolecular Hydrogen-Bonding Networks

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Introduction

A large amount of valuable rubber is used throughout the world and, after its product life, is reused as a thermal energy source. The reason being, semipermanent cross-linking systems such as sulfur vulcanization prohibit reusage as a raw material (fresh rubber). That is, the bond energy of sulfur cross-linking, which is a covalent bond, is too high, preventing its recycling. However, reusage of waste vulcanized rubber as a raw material is an urgent issue for environmental conservation. We need to develop the material recycle method of vulcanized rubber as soon as possible. Although reversible cross-linking system such as Diels−Alder reaction has been investigated, a useful system for practical use has never been found.[1]

Hydrogen bonding has been actively used in supramolecular systems as a means of polymer formation or modification via a self-assembly process.[2−6] Weak and controllable hydrogen bonding leads to bonds with high energy when assembled together. Despite a large number of studies of polymer formation using hydrogen bonds between small molecules or oligomers, very few studies of polymer modification systems using hydrogen bonds between (i) the side chains of polymers or (ii) the side chain of a polymer and a small molecule were investigated. Kato and Frechet have studied a variety of liquid crystalline polymers and found the importance of the interaction between the pyridyl group of small molecules and the pendant aromatic carboxylic acid of polymers.[7−12] Kato and Uryu found new types of liquid-crystalline hydrogen-bonded polymer blends in the system of a main-chain thermotropic polyester containing a lateral pyridyl group and a nonmesogenic poly(4-vinylphenol).[13] Meijer reported supramolecular interaction between (i) the styrene−maleimide alternating copolymer and melamine or (ii) the copolymer of styrene and 2,4-diamino-6-vinyl-1,3,5-triazine can increase high compatibility.[14] Last, Stadler reported the properties of thermoplastic elastomers in which hydrogen bonding of urazol is used to cross-link polybutadiene-based chains; the hydrogen bonding is crucial to the thermal and mechanical properties of these materials.[15−18] None of the above works on supramolecular systems were applicable to industrial applications. Our approach is to investigate the development of themoreversible cross-linking rubber having similar mechanical properties to vulcanized rubber, by using supramolecular hydrogen-bonding networks.

Experimental Section

Addition Reaction of Maleic Anhydride to Polyisoprene (General Procedure).[19] A mixture of 350.0 g (5.14 mol; based on isoprene unit) of polyisoprene rubber (M_w 390 000), 50.3 g (0.514 mol) of maleic anhydride, 3.5 g (0.99 wt % based on polymer) of 6PPD (*N*-phenyl-*N*′-1,3-dimethylbutyl-*p*-phenylenediamine), 54.5 g (0.514 mol) of xylenes, and 35.0 g (9.1 wt % based on polymer) of aromatic oil was mixed at 50 rpm at 90 °C for 20 min in a kneader. The resulting mixture was further kneaded at 50 rpm at 210 °C for 60 min to give the modified polymer (maleated polyisoprene). After the portion of the resulting polymer was dissolved in toluene, the polymer was then precipitated in acetonitrile. The precipitated polymer was washed thoroughly with acetonitrile and dried in vacuo at 60 °C for 3 h. The introduction ratio of maleic anhydride was determined as 5.9 mol % based on isoprene unit by ^1H NMR and IR analysis.

IR (ATR−FTIR): 2961, 2927, 2855, 2726, 1863 (C═O), 1787 (C═O), 1664, 1449, 1376, 1311, 1221, 1128, 1071, 982, 836, 742 cm^{-1}.

^1H NMR (270 MHz, $CDCl_3$) δ in ppm: 5.13 (m, 0.925H, −CH═), 4.90 (m, 0.053H, CH_2═C−), 4.72 (m, 0.024H, CH_2═C−), 2.89−2.56 (m, 0.189H, −CH−, −CH_2−), 2.04 (bs, 3.84H, −CH_2−), 1.68 (s, 2.81H, −CH_3), 1.26 (m, 0.15H, −CH_2−).

DSC analysis (heating rate: 10 °C/min): $T_g = -61.0$ °C.

Addition Reaction of 3-Amino-1,2,4-triazole (ATA) to the Maleic Polyisoprene. A mixture of 350.0 g (0.274 mol; maleic anhydride unit) of maleated polyisoprene, 23.0 g (0.274 mol) of ATA, and 3.65 g (1.5 phr) of 6PPD was kneaded at 50 rpm at 80 °C for 30 min in an internal mixer. The addition of ATA to maleated polyisoprene was identified by IR and solid-state ^{13}C NMR analysis. The introduction ratio of ATA was determined as 5.1 mol % based on isoprene unit by elemental analysis.

IR (ATR−FTIR): 2960, 2925, 2854, 1787 (C═O), 1726 (C═O), 1639 (−NH−CO−), 1596, 1526 (−NH−CO−), 1449, 1376, 1176, 1044, 835, 728 cm^{-1}.

^{13}C NMR(68 MHz, solid-state) δ in ppm: 18.7 (s, CH_2═CH-(CH_3)−), 23.9 (s, CH═C(CH_3)−), 26.5 (s, −CH_2−CH═), 28.6 (s, −CH_2−), 32.0 (s, ═C(CH_3)−CH_2−), 37.7−41.0 (m, −CH_2−, −CH−), 109.0 (bs, −C(CH_3)═CH_2), 111.4 (s, −C(═CH_2)−CH_2−), 125.3 (s, −CH═C(CH_3)−), 135.1 (s, −CH═C(CH_3)−), 149.0 (bs, −N═CH−NH−), 175.8 (bs, −NH−CO−), 185.7 (bs, −COOH).

Elemental analysis. Found: C, 83.40; H, 10.97; N, 2.84; O, 2.79.

DSC analysis (heating rate: 10 °C/min): $T_g = -60.3$ °C.

Preparation of Vulcanized Polyisoprene Rubber. The rubber compounds were prepared in an internal mixer using conventional mixing procedure according to the recipes in Table 1. Vulcanization was performed by heating at 160 °C for 20 min after mixing of vulcanizing agents using an open roll.

Measurement of Properties of Rubbers. Infrared (IR) analyses were performed on a Perkin-Elmer model 2000 FT-IR. ^1H NMR analyses were performed on a JEOL model GSX-270W. Solid-state magic-angle spinning (MAS) ^{13}C NMR spectra were acquired by using single-pulse complete proton-decoupling experiments (pulse saturation) at 68 MHz using a JEOL JNM GSX-270W spectrometer with a commercial 5 mm MAS probe. Glass transition temperature (T_g) was determined by a differential scanning calorimeter (DSC) on a TA instrument model DSC2920. Stress−strain properties were determined at a speed of 500 mm/min on a Shimadzu Autograph AGS-5kNG according to JIS K 6251 using type 3 dumbbells. The viscoelastic properties were measured at room temperature on a Rheometrics dynamic spectrometer, RDS-II, using a parallel-plate test geometry (radius = 25.0 mm). The measurements were carried out with 10 rad/s, a maximum strain of 3%, axial force of −2 g, and temperatures ranging from −100 to 100 °C. Recyclability was evaluated by the capability of re-forming more than 10 times.

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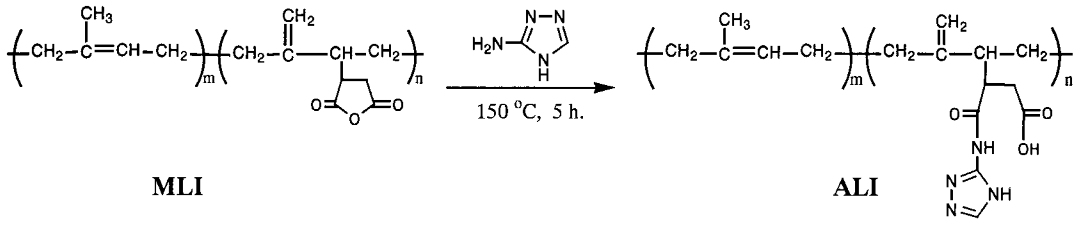
Scheme 1. Synthesis of ALI from MLI



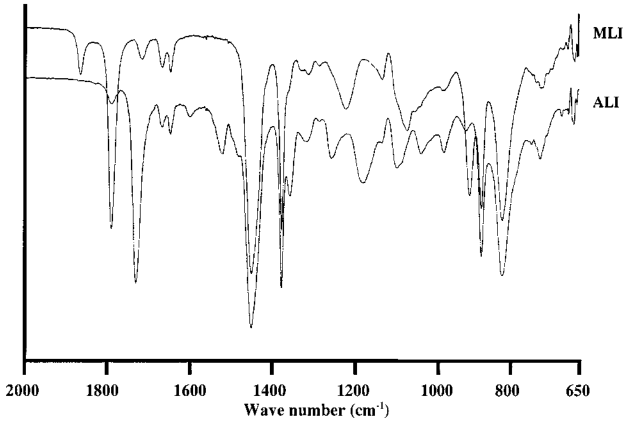


Figure 1. Infrared analysis of MLI and ALI.

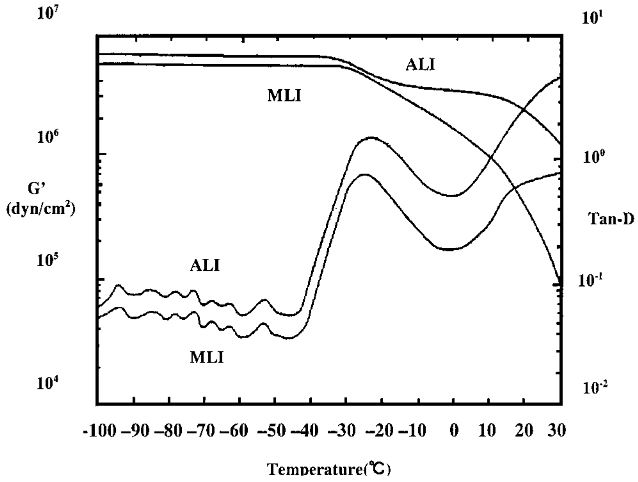


Figure 2. DMA analyses of MLI and ALI. The storage modulus (G') and tan D were measured at 10 rad/s.

Results and Discussion

As a method to introduce hydrogen-bonding moiety to rubber, the addition of active hydrogen compounds followed by modification by maleic anhydride in the solid phase was used. Addition of maleic anhydride to rubber has been widely used in the industry as the easiest method to introduce polar groups.[20,21] Moreover, since the second addition reaction of active hydrogen compounds to cyclic acid anhydride moiety has been known to proceed effectively, the solid mixing reaction of maleic rubber with active hydrogen compounds was expected to proceed effectively. The addition reaction of cyclic acid anhydride and active hydrogen compounds was expected to generate a strong hydrogen-bonding moiety such as carboxylic acid, ester, and amide.

Prior to the synthesis of the themoreversible cross-linking solid rubber, we investigated preliminary reactions of maleic liquid isoprene rubber (MLI) with about 80 types of active hydrogen compounds such as amines, alcohols, and thiols.

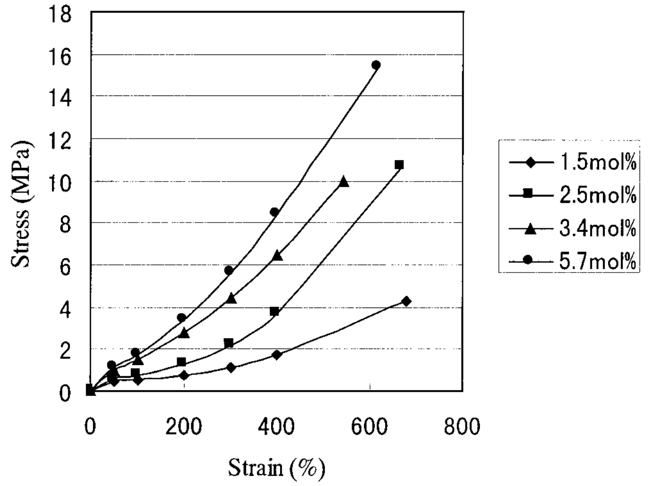


Figure 3. Stress−strain curves of TRI with various introduction ratio.

Table 1. Physical and Recycle Properties of Polyisoprene and TRI

run	1	2	3	4	5	6
polyisoprene[a]	100	100	100			
TRC-IR (3.8 mol %)[b,c]				100	100	
TRC-IR (5.1 mol %)[b,c]						100
carbon black	30		30		30	30
aromatic oil	8.7	8.7	8.7	8.7	8.7	8.7
zinc oxide		5	5			
stearic acid		3	3			
6PPD[d]	2	2	2	2	2	2
TBBS[e]		1	1			
sulfur		2	2			
stress−strain properties						
100% modulus (MPa)	0.24	0.64	1.32	0.48	1.64	1.72
300% modulus (MPa)	0.20	1.35	6.10	0.91	4.86	5.61
tensile strength (MPa)	027	25.00	30.14	1.51	9.85	15.39
elongation at break (%)	572	646	630	414	519	616
recyclability[f]	OK	NG	NG	OK	OK	OK

[a] M_w 390 000. [b] Thermoreversible csoss-linking rubber. [c] Introduction ratio was determined by elemental analysis. [d] *N*-Phenyl-*N'*-1,3-dimethylbutyl-*p*-phenylenediamine. [e] *N*-*tert*-Butyl-2-benzothiazylsulfenamide. [f] Re-forming ability more than 10 times.

Among these active hydrogen compounds, heterocyclic amines gave higher viscosity. In particular, 3-amino-1,2,4-triazole (ATA) solidified the liquid rubber at room temperature. This was attributed to cross-linking by strong hydrogen bonds between the amide triazole−carboxylic acid units of rubber chains. The reaction of the amine group of ATA and the acid anhydride ring was confirmed by ^{1}H NMR and IR analyses. The introduction of ATA to MLI was identified by the conversion of the absorption peaks of acid anhydride at 1864 and 1788 cm^{-1} to the peaks of amide at 1635 and 1526 cm^{-1}. Although the concentration of hydrogen-bonding units was low, the absorption peak of carboxylic acid was observed at a lower region (1728 cm^{-1}) than that of general carboxyl acid (1760 cm^{-1}), indicating

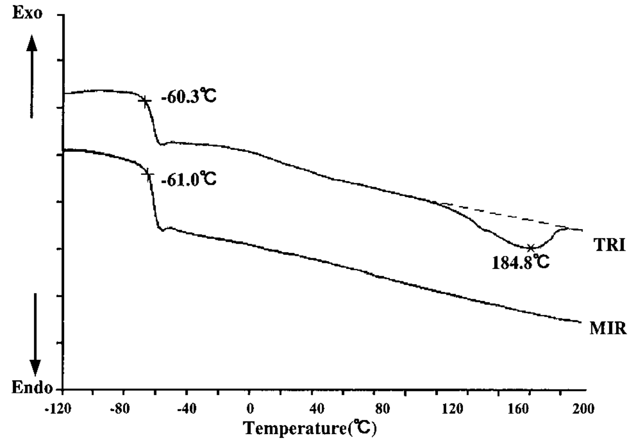


Figure 4. DSC analyses of TRI and MIR.

strong hydrogen bonds between the amide triazole–carboxylic acid units.

The viscosity of the resulting modified liquid rubber (ALI) was much higher than that of MLI as shown in Figure 2 (dynamic mechanical properties). The storage modulus (*G′*) and tan *D* at 10 rad/s are shown for MLI and ALI. In the storage modulus curve of ALI, the transition to flow is shifted to a 50 deg higher temperature, and the rubbery plateau is clearly observed. A tremendous change in the mechanical properties was observed compared to the case of MLI.

On the basis of the result of the preliminary reactions, we synthesized themoreversible cross-linking solid rubber. An addition reaction of maleic anhydride to solid isoprene rubber was achieved through a kneading process at 50 rpm at 210 °C for 60 min. By the prekneading process with xylenes and an aromatic oil as a reaction activator and an antioxidant, maleic anhydride could be effectively grafted into polyisoprene with the deterioration of polyisoprene being suppressed. The introduction ratio could be changed by controlling the reaction time, reaction temperature, and the amount of maleic anhydride. The highest introduction ratio was 7.5 mol % when 10 mol % of maleic anhydride was used.

The second introduction reaction of 3-amino-1,2,4-triazole (ATA) to the resulting maleic polyisoprene was

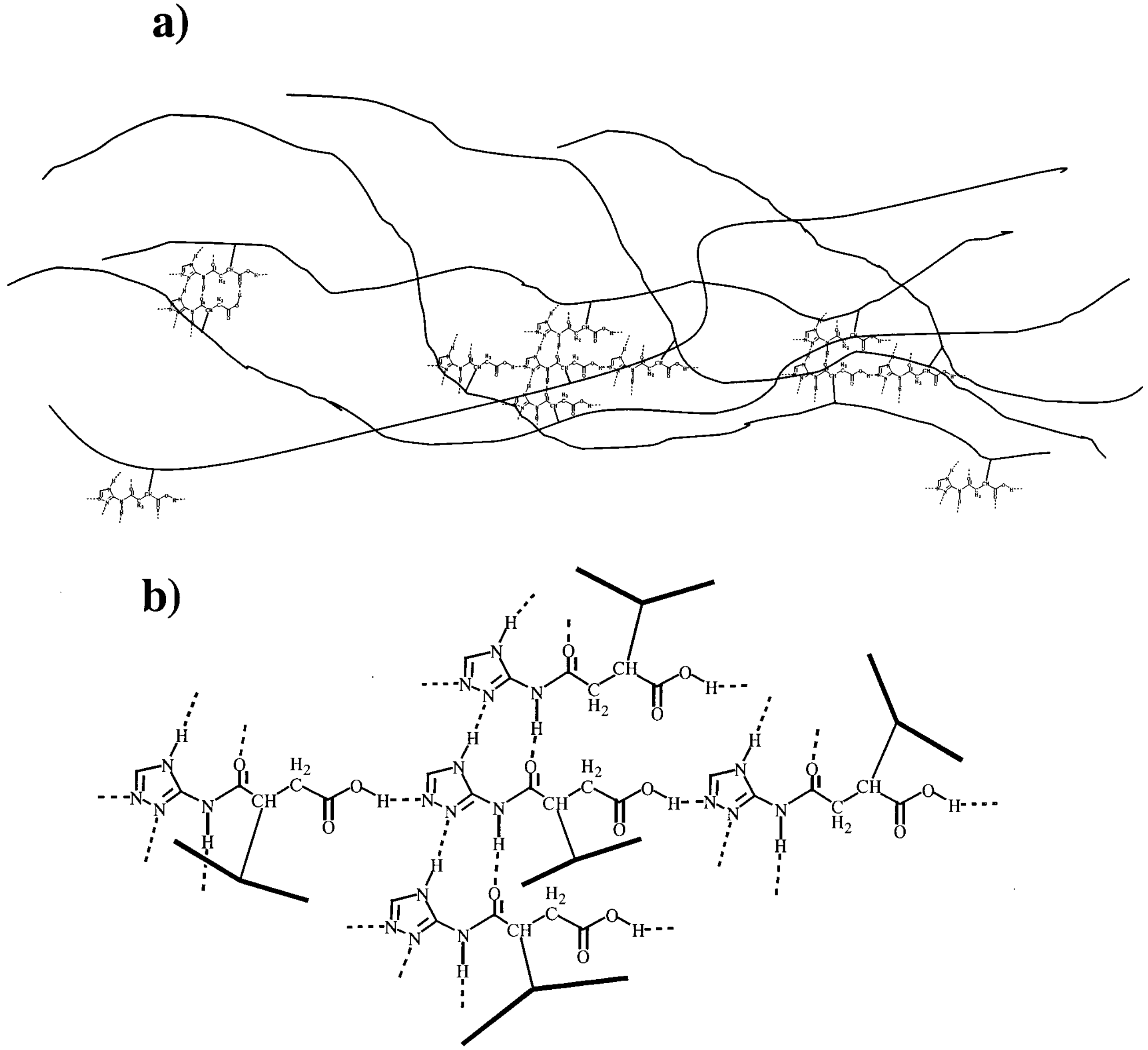


Figure 5. (a) Speculated model of rubber structure. (b) Speculated model of cross-linking moiety (six-point hydrogen bonding).

easily achieved by kneading at 50 rpm at 80 °C for 30 min.

The properties of the obtained rubber (TRI) are shown in Table 1.

The mechanical properties of TRI (3.8 mol %) (run 4) are much higher than those of uncured IR containing 30 phr (parts per hundred rubbers) of carbon black (CB) (run 1). Although 100% and 300% moduli of TRI without CB (run 4) were slightly lower than those of sulfur-cured IR (run 2), the tensile strength and elongation at break were much lower than sulfur-cured IR without CB. However, the mechanical properties of TRI (5.1 mol %) containing 30 phr of CB were sufficiently high (run 6). Although the tensile strength and elongation at break were lower than CB-filled vulcanized rubber (run 3), the moduli were as high as those of sulfur-cured rubber. The mechanical properties of the resulting rubber were similar to those of sulfur-vulcanized rubber, clearly separating from general thermoplastic elastomers (e.g., SEBS). Figure 3 also shows the absence of creep phenomenon, which is typical to general thermoplastic elastomers and also Stadler's erastomer.[15−18] This result indicates the possibility that the hydrogen-bonding units have sufficient high energy. CB-filled TRC-IR seems to be a good substitute for CB-filled vulcanized rubber in practical use. Re-forming of the TRC-IR could be repeated more than 10 times without changing its various properties. This result proves that its recyclability is satisfactory in practical use.

The stress−strain curves at a strain rate of 500 mm/min for a series of samples with various degrees of substitution are shown in Figure 3. The stress at any given strain increased with the increase of the introduction ratio, which indicates an increase in the hydrogen-bonding cross-link moiety.

The glass transition temperature (T_g) of the modified polyisoprene observed by differential scanning calorimetry (DSC) was almost the same as that of the starting polyisoprene. In addition to the glass transition, the modified polyisoprene show a second endothermic transition around 185 °C in the DSC curve as shown in Figure 4. This may indicate the cleavage of the hydrogen bonding.

The structure of the hydrogen-bonding network is speculated as shown in Figure 5a. Theoretically, the hydrogen-bonding moiety (amide triazole−carboxylic acid unit) generated by the addition reaction of ATA and acid anhydride can form a six-point hydrogen-bonding structure as shown in Figure 5b. The six hydrogen bonds should produce a strong cross-linking moiety.

We are now investigating the crystal X-ray analysis of a model compound generated by the addition reaction of succinic anhydride and ATA. The actual structure of the hydrogen-bonding moiety will be made clear in the near future.

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