Liquid Isoprene Rubber for UV Curing Applications

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Abstract

UV curable liquid isoprene rubber (UC-LIR) is commercialized by our unique polymerization and polymer modification technology. UC-LIR contains methacryloyl groups on polyisoprene main chain and it is curable by UV irradiation in the presence of photoinitiator. It gives UV-cured materials with remarkable flexibility compared with urethane acrylate or polybutadiene acrylate. Pressure sensitive adhesives (PSAs) using UC-LIR indicates distinguished cohesion at high temperature and excellent adhesiveness. UC-LIR is expected to be applied for adhesives for electronic equipment, sealants for display or PSAs from its unique properties. And we have also developed epoxidized liquid isoprene rubber (E-LIR) that is curable by UV cationic polymerization.

1. Introduction

Radiation technology is widely used in the field of adhesives, coatings, sealants and inks from viewpoints of reducing volatile organic compounds and manufacturing energy1). And it is an important characteristic curing at lower temperature than thermosetting resins such as epoxy resin. Thus, base materials can keep its shape during radiation and it achieves precision adhesiveness.

On the other hand, thinned adhesive and sealant layers are required in the electronics market because precision components have been getting smaller and thinner2). These electronic components are often exposed to high temperature during production process, or the use of electronic components generates heat. Thus, flexibility is also required to reduce the stress generated by heat expanding of base materials. However, most of acrylic monomers and oligomers gave hard materials after curing and it was difficult to achieve enough flexibility. In this paper, authors designed new UV curable materials that gave excellent rubber elasticity after curing.

2. Results and Discussion

2-1. Molecular design

Liquid polybutadiene (meth)acrylate has been commercialized by some companies as a UV curable material3). Liquid polybutadiene is a hydrophobic oligomer that is composed of only hydrocarbon units, and its cured material shows excellent water resistance, moisture resistance, insulating properties, chemical resistance, transparency and toughness. On the other hand, it is well known that polyisoprene shows much better flexibility and tackiness than polybutadiene4). Therefore, we have developed UV curable polyisoprene for adhesives and pressure sensitive adhesives.

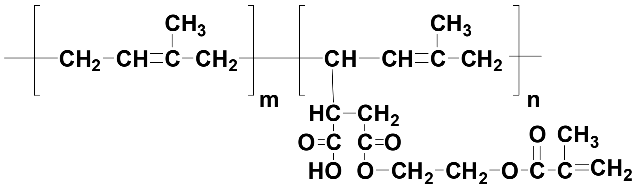


Figure 1. Molecular structure of UC-LIR

Main factors affecting cured properties are molecular weight, microstructure of polyisoprene (1,4-structure, 3,4-structure), bonding position of functional groups (terminal or side chain) and functionality. And optimization of these factors gave excellent flexibility. Molecular structure of UC-LIR is shown in Figure 1 and its characteristics are summarized in Table 1.

Table 1. Characteristics of UC-LIR

Grade	UC-203	UC-102	UC-105*)
Molecular Weight	36000	19000	19000
Methacryloyl groups	3 units / chain	2 units / chain	5 units / chain
Methacrylate Equivalent (g/eq)	6700	5900	2200
Melt Viscosity (Pa.s:38^{0}C)	160	30	70
Appearance	Transparent and Slightly yellow	Transparent and Slightly yellow	Transparent and Slightly yellow

*) Developing grade

2-2. Typical properties

Typical properties of UC-LIR, polybutadiene acrylate (PBd-Ac) and urethane acrylate (Ur-Ac) are shown in Table 2. UV curable materials containing 3 wt% of DAROCUR1173 (Ciba Specialty Chemicals Inc.) were sandwiched with 50μmt polyester film with 0.8mmt plastic mold. And sample sheets were prepared by UV irradiation using a high-pressure mercury lamp (light intensity: 64mW/cm^2) at room temperature, and it gave 2700mJ/cm^2 of UV energy. Glass transition temperature (Tg) of cured sheets was measured by differential scanning calorimeter (DSC6200, Seiko Instrument Inc). Shrinkage ratio was determined by comparing density before and after curing. Pieces for tensile test (50 x 6 x 0.8mm) were prepared from cured sheets, and tensile test was carried with Instron5566 (Instron Japan Company Limited). Hardness was determined with a type A durometer.

Table 2. Typical properties of UV curable materials

Grades	Mn	Viscosity	Tg	Shirinkage Ratio	Tensile Strength	Tensile Elongation	Hardness
	(g/mol)	(Pa.s :38^{0}C)	(^{0}C:DSC)	(%)	(MPa)	(%)	(Type-A)
UC-203	36000	160	-60	0.5	0.4	111	32
UC-102	19000	30	-61	1.2	0.3	106	25
UC-105	19000	70	-58	1.5	0.7	29	61
PBd-Ac-1	1000-5000	700	-15	3.4	10.9	51	98
PBd-Ac-2	1000-5000	3	-72	2.6	1.1	32	66
Ur-Ac-1	5000-10000	50	-30	2.2	2.5	53	78
Ur-Ac-2	5000-10000	110	-36	1.5	2.1	80	68

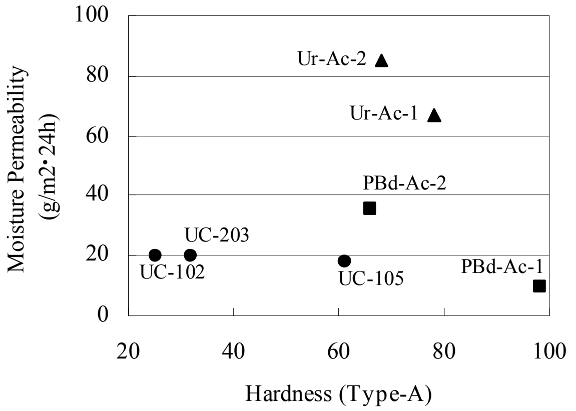


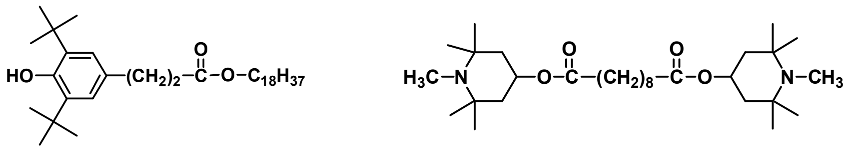
Figure 2. Moisture permeability and hardness of UV cured materials.

UC-LIR indicated higher elongation and lower hardness than polybutadiene acrylate or urethane acrylate. And UC-LIR can keep its own flexibility over wide range of low temperature, due to its low Tg. Besides, it showed distinguished low shrinkage ratio.

Moisture permeability of UV cured sheets was measured by thermo-hygrostat controlled at 40 ^{0}C and relative humidity 90% (Figure 2). UC-LIR showed excellent moisture-permeability resistance and flexibility. It is suitable for precision adhesives for electronics such as sealants for Liquid Crystal Display or organic Electro Luminescent Display that is so sensitive to moisture.

2-3. Heat resistance

Generally, polyisoprene does not have enough heat resistance because double bonds of polyisoprene are unstable to heat, and cross-link or decomposition reaction occurs5). Thus, a large number of antioxidants have been developed to improve heat resistance of polyisoprene, and hindered phenol is well known as an effective antioxidant6). However, we found that hindered amine light stabilizer (HALS) is more effective than hindered phenol to improve heat resistance of cured UC-LIR (Figure 4, 5). Test pieces were prepared from following compound (UC-203/ dicyclopentanyl acrylate/ DAROCUR1173/ antioxidant = 50/ 50/ 3/ 0.5 wt) and put into thermostatic chamber at 100 ^{0}C under air. In the case of compound without antioxidant, tensile modulus increased after 72 hours by hardening degradation, and its appearance changed to brown. Hindered phenol (IRGANOX1076) could keep the cured compound low modulus in 240 hours but its appearance changed to yellow soon. On the other hand, hindered amine (TINUVIN765) could keep it flexible in 960 hours without changing color.



IRGANOX1076 **TINUVIN765**

Figure 3. Structures of antioxidants

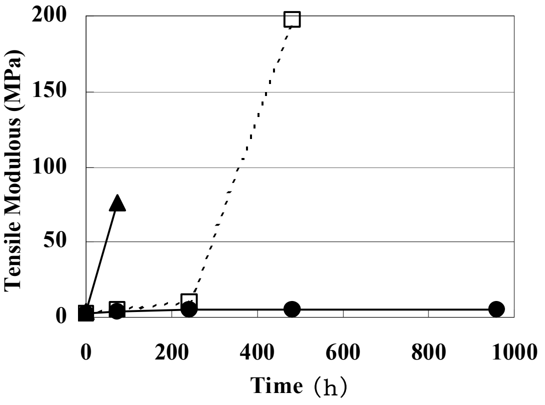


Figure 4. Effect of antioxidant on tensile modulus at 100 ^{0}C.

—▲— None
- -□- - IRGANOX1076
—●— TINUVIN765

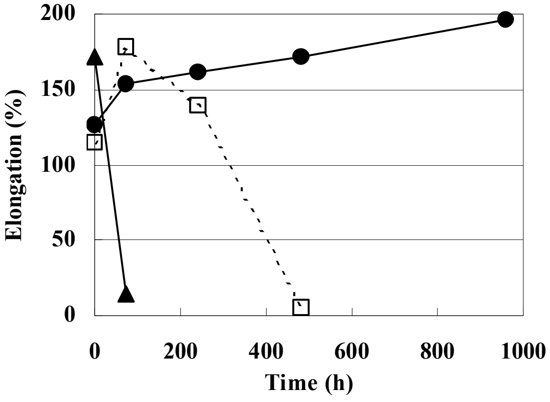


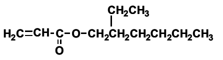
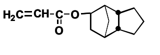
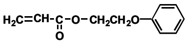
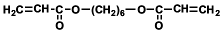
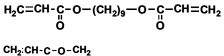
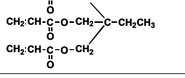
Figure 5. Effect of antioxidant on tensile elongation at 100 ^{0}C.

—▲— None
- -□- - IRGANOX1076
—●— TINUVIN765

2-4. Properties of UV cured compound composed of UC-LIR and acrylic monomers

Compatibility of UC-LIR with some (meth)acrylic monomers is shown in Table 3. It indicates excellent compatibility with low polar acrylic monomers such as alkyl mono-acrylates, cycloaliphatic mono-acrylates and long chain di-acrylates. However, compatibility with multi-functional acrylates is not good, because UC-LIR is low polar material that comes from polyisoprene structure.

Table 3. Compatibility of UC-LIR with acrylic monomers.

Monomers	Structure	UC-203	UC-102	UC-105
2-Ethylhexyl acrylate	 $H_2C{=}CH{-}\underset{O}{\underset{\|}{C}}{-}O{-}CH_2\overset{CH_2CH_3}{\overset{\vert}{C}H}CH_2CH_2CH_2CH_3$	Excellent	Excellent	Excellent
Dicyclopentanyl acrylate		Excellent	Excellent	Excellent
Phenoxyethyl acrylate		good	good	good
1,6-Hexanediol diacrylate	 $H_2C{=}CH{-}\underset{O}{\underset{\|}{C}}{-}O{-}(CH_2)_6{-}O{-}\underset{O}{\underset{\|}{C}}{-}CH{=}CH_2$	Poor	Poor	Excellent
1,9-Nonanediol diacrylate	 $H_2C{=}CH{-}\underset{O}{\underset{\|}{C}}{-}O{-}(CH_2)_9{-}O{-}\underset{O}{\underset{\|}{C}}{-}CH{=}CH_2$	Excellent	Excellent	Excellent
Trimethylolpropane triacrylate		Poor	Poor	Poor

Effect of adding di-acrylate on curing speed of UC-102 is shown in Figure 6. Compounds comprised of UC-102, 1,9-nonanediol diacrylate (NDDA, SHIN-NAKAMURA CHEMICAL CO., LTD, A-NOD-N) and 3 wt% of DAROCUR1173 were sandwiched between polyester films with 0.8mmt plastic mold. After UV irradiation, the conversion of compounds was calculated by gel fraction insoluble in toluene. In the result, the compound containing more NDDA indicated higher curing speed.

Effect of adding dicyclopentanyl acrylate (DCPA, Hitachi Chemical Co., Ltd., FA-513A) on physical properties of UC-203 is shown in Figure 7. Although UV cured UC-203 showed excellent elongation, its tensile strength was very low. On the other hand, cured DCPA gave less elongation and it was easy to break. Compound comprised 75 wt% of DCPA and 25 wt% of UC-203 showed excellent elongation and tensile strength. UC-203 is superior to improve toughness of hard type UV curable ingredients because it is a rubber elastic material.

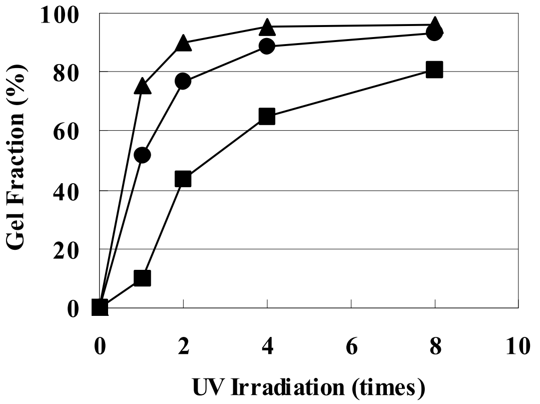


Figure 6. Effect of adding NDDA on curing speed of UC-102. Light intensity: 40mW/cm^2. Irradiation energy (1 time): 188mJ/cm^2.

—▲— UC-102/ NDDA = 50/ 50

—●— UC-102/ NDDA = 75/ 25

—■— UC-102/ NDDA = 100/ 0

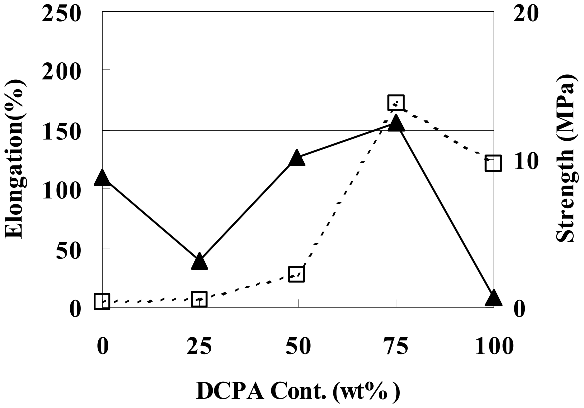


Figure 7. Effect of adding DCPA on physical properties of UC-203. Light intensity: 64mW/cm^2. Irradiation energy: 2700mJ/cm^2.

—▲— Elongation

- □ - Strength

2-6. Pressure sensitive adhesives aplication

Characteristics of pressure sensitive adhesives (PSAs) based on UC-203 are shown in Table 4. PSAs solutions are prepared from following compounds (UC-203/ tackifier resin/ DAROCUR1173/ IRGANOX1010 = 100/ 20/ 5/ 0.3 wt) at 30 wt% solids in toluene. After each solution was coated on polyester film and dried at 100 ^{0}C for 5 minutes, UV irradiation was carried out under air (3675mJ/cm^2). PSAs based on UC-203 showed excellent cohesion compared with hot melt PSAs based on natural rubber or SIS. And its productivity is much better than acrylic PSAs that need a few days for cross-link reaction because UV cross-link is carried out in a few minutes.

Table 4. Characteristics of pressure sensitive adhesives based on UC-203

Formulation		1	2	3	4
UC-203		100	100	100	Acrylic PSA
YS resin TO-105[1]		20			
Clearon M-115[2]			20		
PINECRYSTAL KE-100[3]				20	
DAROCUR1173		5	5	5	
IRGANOX1010		0.3	0.3	0.3	
Coating Thickness	(μm)	30	28	28	44
Ball Tack(at 25 ^{0}C)		7	3	5	6
60 ^{0}C Creep test					
Holding Power	(min)	240<	240<	240<	240<
Slippage	(mm)	1.0	0.9	0.2	4.3
180°Peel test					
to Stainless	(N/m)	955	1200	1270	540
to PE	(N/m)	155	108	93	240

1)Aromatic modified terpene resin (YASUHARA CHEMICAL Co., Ltd.)
2)Aromatic modified hydrogenated terpene resin (YASUHARA CHEMICAL Co., Ltd)
3)Hydrogenated rosinester resin (ARAKAWA CHEMICAL INDUSTRIES LTD.)

2-7. Development of epoxidized liquid isoprene rubber (E-LIR)

Most of UV curable resins are cured by radical curing with (meth)acrylic monomers or oligomers as described above. Recently, UV cationic curing system has also been studied because it does not inhibited by oxygen and gives excellent physical properties[7]. Epoxy, vinyl ether and oxetane compounds have already been commercialized as UV cationic curable resins, but a number of that compounds is much smaller than UV radical curable resins[8]. And it had been difficult to obtain enough flexibility by UV cationic curing system. We have developed epoxidized liquid isoprene rubber (E-LIR) that contains polyisoprene structure as well as UC-LIR (Figure 8, Table 5).

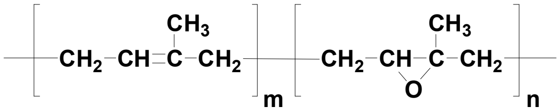
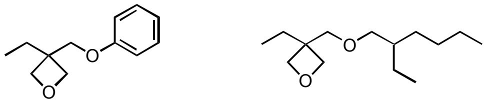


Figure8. Molecular structure of e-LIR



OXT-211 **OXT-212**

Figure9. Structure of oxetane monomers (TOAGOSEI CO LTD.)

Table5. Characteristics of E-LIR

Grade	KL-610*)	KL-613*)	KL-630T*)
Molecular Weight	36000	19000	36000
Epoxy Equivalent (g/eq)	2000	2000	667
Tg (^{0}C: DSC)	-59	-59	-51
Melt Viscosity (Pa.s:38^{0}C)	160	30	70
Appearance	Transparent and Slightly yellow	Transparent and Slightly yellow	Transparent and Slightly yellow

*) Developing grade

UV curable following compounds were sandwiched between polypropylene films with 0.8mmt plastic mold. And sample sheets were prepared by aging at 60 ^{0}C for 1 hour after UV irradiation (938mJ/cm^2). Water absorptivity was determined by comparing weight before and after sousing them into water at 25 ^{0}C for 24 hours.

E-LIR showed much better flexibility and lower water absorptivity than commercially available epoxidized polybutadiene when oxetane monomers were added as diluents (Figure 9, Table 6).

Table6. Properties with oxetane monomers

entry	1	2	3	4	5	6
KL-610	50	50				
KL-630T			50	50		
Epoxidized PBd					50	50
OXT-211	50		50		50	
OXT-212		50		50		50
Irganox1010	0.1	0.1	0.1	0.1	0.1	0.1
Rhodorsil-2074[1)]	0.5	0.5	0.5	0.5	0.5	0.5
Tensile Strength(MPa)	0.60	0.47	1.08	0.80	26	6.8
Tensile Elongation(%)	211	112	82	53	40	30
Hardness (Type-A)	30	30	55	46	98	90
Water Absorptivity (%)	0.11	0.03	0.06	0.05	0.32	0.24

1) UV cationic photoinitiator (Rhodia)

3. Conclusion

UV curable liquid isoprene rubber represents a novel class of elastic UV curable resin. It gave remarkable flexibility and moisture resistance compared with common UV curable materials. And hindered amine light stabilizer enhanced heat resistance and color stability of compounds containing UV curable liquid isoprene rubber. These performances are suitable for precision adhesives for electronics and pressure sensitive adhesives.

4. Reference

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