

Properties of products cured by crosslinking of alkyl vinyl group of 1,2-Polybutadiene and 1,2-SBS

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ABSTRACT

In recent years, thermosetting resins have been used in various applications because of the ease in controlling viscosity before hardening, compared with thermoplastic resins, as well as their superior handling. However, the various types of monomers, resins, and methods contributing to hardening in diverse applications have increased the complexity of the resin systems. To obtain a hardened product with physical properties close to its designated purpose, it is necessary to understand the properties of the monomers and resins that contribute to hardening, as well as their hardening mechanisms, and to perform appropriate curing. The crosslinking (hardening) of alkyl vinyl groups explained in this section has been increasingly utilized recently for fabricating electronic materials with low dielectric properties and insulation, as well as for preparing rubber modifiers with enhanced mechanical strength, water resistance, and oil resistance.

In this section, we explain thermal hardening, or curing, of monomers and resins containing an alkyl vinyl group and provide some examples.

INTRODUCTION

The lowest unoccupied molecular orbital (LUMO) energy level in the ethylene group is high, and the reaction of unsubstituted ethylene in which the LUMO is involved is unlikely to occur⁽¹⁾. Therefore, a concerted reaction is proposed to lower the LUMO level by coordinating an electron-withdrawing group to ethylene. Typical examples are 2+2 cycloaddition reactions and 2+4 reactions (Diels–Alder reaction)⁽²⁾⁽³⁾. However, an ethylene group having an unsubstituted ethylene and an electron-donating group has a high energy level (Fig. 1) and extremely low photoreactivity (Fig. 1. Ethylene absorbs light and is excited to the LUMO). On the other hand, a concerted thermal reaction in which the ethylene group having an electron-donating group was thermally excited has also been reported; however, the reaction requires a temperature of 230 °C or higher⁽⁴⁾.

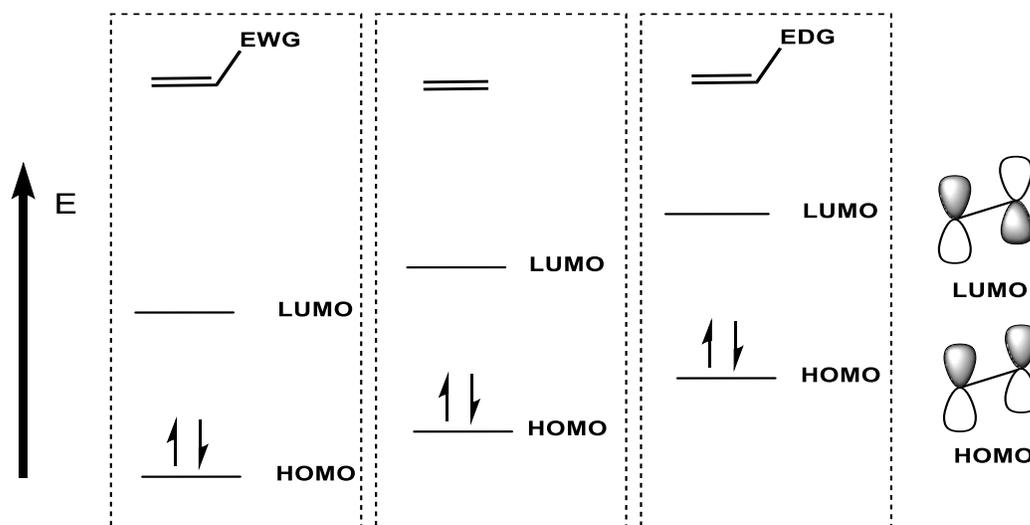


Figure 1. Energy level of ethylene group

(EWG: electron-withdrawing group, EDG: electron-donating group)

Although crosslinking (hardening) through such a concerted reaction is useful as a synthesis method, this method is not practical for industrial purposes because it follows the orbital symmetry rules (Fig. 1. Phase overlap of the white and black ellipses of the HOMO and LUMO)⁽²⁾ and involves a reaction at a high temperature. The crosslinking (hardening) of the ethylene group by a nucleophile or electrophile is also not practical because the initiator is less stable, and the crosslinking conditions are strictly controlled⁽⁵⁾. Therefore, conditions for the easy control of crosslinking reactions (hardening), i.e., thermal crosslinking at approximately 100°C with a radical initiator and photocrosslinking at room temperature, have been investigated for a long time⁽⁶⁾. One of these conditions is the crosslinking of a representative ethylene compound such as an acrylic acid ester. In this method, materials (monomers) in which the energy level was lowered by replacing the electron-withdrawing acryl group with ethylene is mixed with a crosslinking initiator to generate radicals in response to light and heat (this is a radical reaction involving a singly occupied molecular orbital: the energy level between HOMO and LUMO). This method rendered the crosslinking of ethylene groups easier to control in both the photoreaction and thermal reaction. Moreover, this method was examined as a hardening method for industrial purposes and has been implemented for practical applications. Although the acryl group is advantageous for easily obtaining the hardened products, their polarity is high because the ester groups are themselves included in the hardened products. Therefore, their dielectric character and water resistance are disadvantageous for the material properties. Another disadvantage is their low compatibility with materials with low polarity, such as rubber.

Therefore, ethylene groups having no polar group, i.e., a hardened product produced by the crosslinking of alkyl vinyl group, are in high demand in the fields of electronic materials and rubber elastomers. In particular, highly insulating and low-dielectric materials have been developed in recent years as electronic materials for communication, and resins hardened with low-polarity hydrocarbon materials have mainly been used for this purpose. Polybutadiene has been widely used as an alkyl vinyl material having no polar group, and its demand has increased in recent years⁽⁶⁾⁽⁷⁾.

The hardening of polybutadiene having an alkyl vinyl group is discussed in the next section.

EXPERIMENTAL DETAILS

Figure 2 shows the structure of polybutadiene, a typical compound with an alkyl vinyl group. Polybutadiene is a polymer derived from 1,3-butadiene. There are two regioisomers that depend on the polymerization position (Fig. 2: m and n).

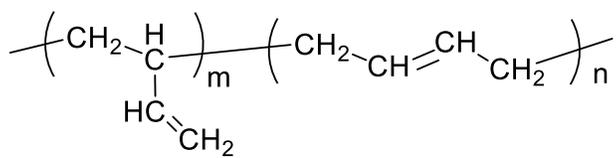


Figure 2. Structure of Polybutadiene [Poly(1-butene-co-2-butene)]

The 1,2-vinyl group and 1,4-olefin of polybutadiene have high energy levels because they have an electron-donating group (alkyl substitution; Fig. 1). The electron-donating effects of the 1,2-vinyl group of 1,2-polybutadiene and 1,4-olefin of 1,4-polybutadiene are significantly different. Because polybutadiene having 1,2-vinyl groups is obtained by monoalkyl substitution, its energy levels are lower than those of the dialkyl-substituted 1,4-olefins and it exhibits higher crosslinking reactivities. This higher crosslinking reactivity of 1,2-polybutadiene over 1,4-polybutadiene can also be explained from steric factors ([1] and [2])⁽⁹⁾.

[1] The vinyl group is one carbon away from the main chain and is exposed (Fig. 3).

[2] Upon reaction, steric hindrance is overcome by the rotation of the vinyl group (arrow in Fig. 3).

Because 1,2-polybutadiene exhibits a higher crosslinking reactivity than 1,4-polybutadiene, it has been used for the crosslinking of alkyl vinyl groups and implemented in practical applications.

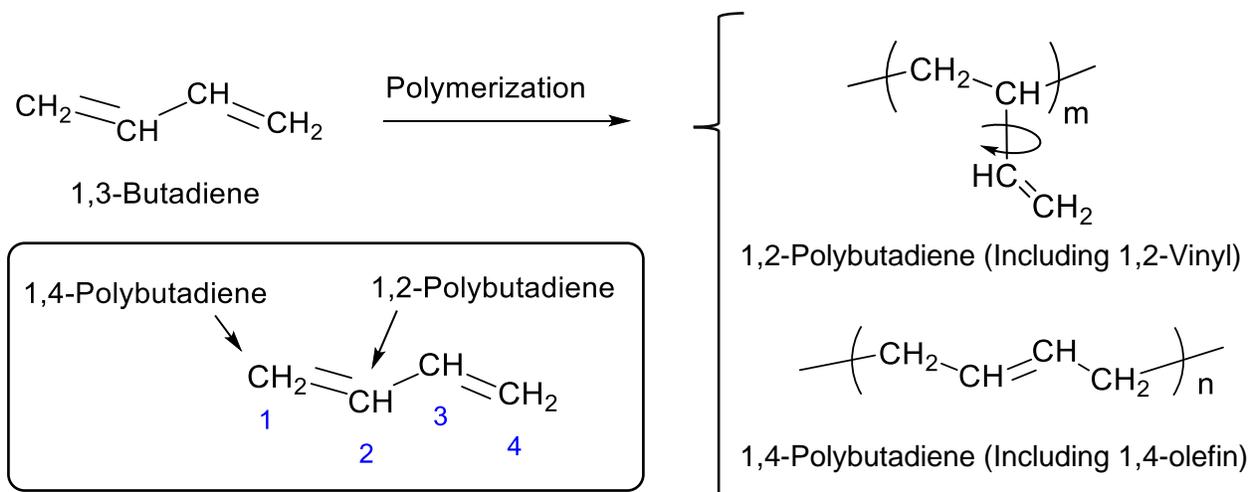


Figure 3. Geometric isomers of Polybutadiene

As previously mentioned, because the energy level of polybutadiene containing no electron-withdrawing group is high, the photocrosslinking reaction rarely proceeds. Thus, a method in which the crosslinking proceeds via the generation of radical species in a heated state has been studied. In other words, in this method, polybutadiene and a thermal radical generator are added to the rubber and resin and then heated to realize crosslinking. The rubber and hardened resins obtained by this crosslinking reaction have a three-dimensional network, which improves the elasticity, strength, oil resistance, and water resistance⁽⁶⁾⁽⁸⁾⁽⁹⁾.

For thermal radical crosslinking (hardening) of polybutadiene, peroxides (e.g., dicumyl peroxide [DCP]) are used⁽¹⁰⁾. Peroxides generate radicals in a specific temperature range (Fig. 4: 110–130°C for DCP; 10 h half-life, temperature 116°C), which promote the crosslinking (hardening) of a vinyl group⁽¹⁰⁾.

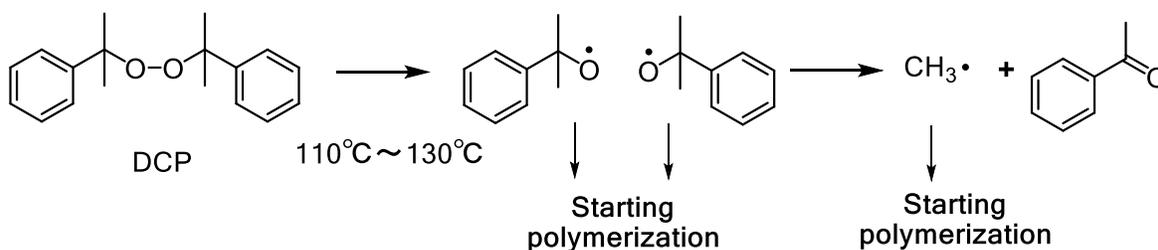


Figure 4. Radical formation mechanism of DCP*

*2-Phenyl-2-[(2-phenylpropan-2-yl)peroxy]propane

The 1,2-vinyl group and olefin in polybutadiene differ in terms of reactivity and properties of hardened products according to their content. Table 1 shows the relationship between the hardened products and glass transition temperature.

Table 1. 1,2-Vinyl group content of Polybutadiene and Glass transition temperature of Cured resin

Polybutadiene		Cured resin
m (1,2-vinyl) / n	M _n	T _g
92 / 8	3,200	54°C
66 / 34	2,700	17°C
44 / 56	2,500	Poor curing

Experimental method

Compound ratio, Polybutadiene: DCP = 100:3 (phr)

The mixture containing polybutadiene was poured into a mold to harden it under the conditions stated below.

Hardening conditions: 110°C × 3 h → 150°C × 3 h; thickness 1 mm.

The higher the vinyl content, the higher is the glass transition temperature (T_g) of the hardened product (Table 1). This is correlated with the crosslinking density of the vinyl group in the hardened composition.

RESULTS AND DISCUSSION

1. Styrene-butadiene-styrene copolymer (SBS)

The SBS copolymer is considered as an example.

Styrene-butadiene-styrene copolymer (SBS)

SBS contains butadiene units. Similar to polybutadiene, these butadiene units have regioisomers of the 1,2-vinyl group and olefin (Fig. 3). Their structures are as follows: the styrene and butadiene units are coordinated in a block shape (mass) (Fig. 5) and are randomly coordinated (Fig. 6: Random SB). The physical properties of each cured product are listed in Table 2.

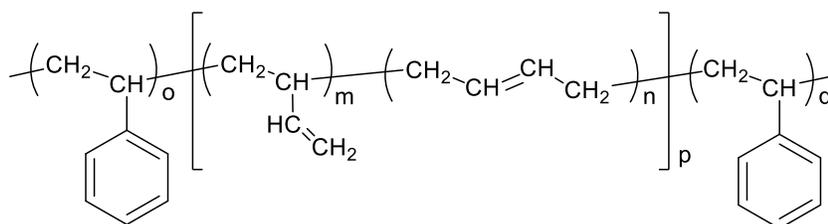


Figure 5. SBS [Poly (styrene-*block*-butadiene-*block*-styrene)]

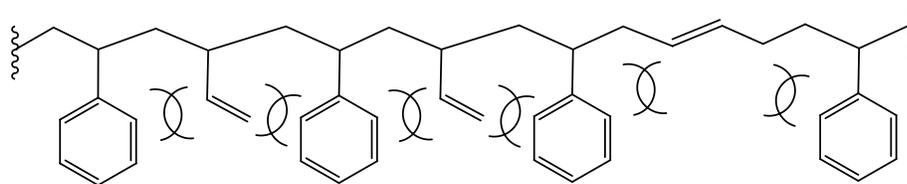


Figure 6. Randomly placed SB [Poly (styrene-*ran*-butadiene)]

Table 2. 1,2-Vinyl group content of styrene-butadiene-styrene copolymer and Glass transition temperature of Cured resin

Polymer containing styrene-butadiene				Cured resin
Ratio of Styrene /Butadiene	Ratio of butadiene (p) m (1,2-Vinyl) / n	M _n	Orientation o/(m,n)/p	T _g
o / p / q = 10 / 80 / 10 ^{a)}	92 / 8	5,000	Block	72°C
o / p / q = 10 / 80 / 10 ^{a)}	55 / 45	5,000	Block	Poor curing
Styrene/Butadiene =20 / 80 ^{b)}	90 / 10	5,000	Random	13°C

Experimental method

Compound ratio, Polybutadiene: DCP = 100:2 (phr)

The mixture of copolymers containing styrene and butadiene was poured into a mold to cure under the conditions stated below.

Curing conditions: a) 200°C -210°C × 2 h; thickness 0.5mm.

b) 80°C × 1 h → 150°C × 2 h; thickness 1 mm.

Random SB (Fig. 6) shows that the positions of styrene and butadiene units are not controllable. The butadiene units are subject to the steric impact of the adjacent styrene units, which hinder the progression of crosslinking. However, for the blocked SBS, the butadiene units are continuously positioned away from the styrene units (Fig. 5). Consequently, the former is not subject to the steric hindrance from the styrene units. Therefore, block-copolymerized SBS (1,2-vinyl content 92%; 1,2-SBS) shows high crosslinking reactivity⁽⁸⁾ and, consequently, the glass transition temperature (T_g) of the cured products is high.

The T_g of the block-oriented SBS cured product is correlated with the 1,2 vinyl group content (Table 2, m/n ratio). This may be due to the crosslinking density of the vinyl group contained in the hardened product, as evident from Table 1.

2. Double bonds remaining in the cured resin

The double bonds in polybutadiene (1,2-vinyl group, 1,4-olefin) may remain so, not undergoing crosslinking, in the hardened product. This is because some double bonds do not undergo crosslinking (curing) due to the decreased mobility of the molecules owing to the progression of the crosslinking (curing) reaction. These residual double bonds may participate in oxidation reactions over time and change the physical properties of the hardened product. The oxidation of such products is more likely to occur in 1,4-olefins⁽⁸⁾. This can be inferred by comparing the initiation temperature of oxidation (Fig. 3)

Table 3. Oxidation start temperature of 1,2-Polybutadiene and 1,3-Polybutadiene

	1,2-Polybutadiene (1,2-vinyl content :92%, $M_n=3,200$)	1,4- Polybutadiene (1,2- vinyl content :44%, $M_n=2,100$)
Oxidation start temperature	174°C	150°C

Measurement method: TG/DTA in Air

Table 4. Enthalpy Comparison of 1,2-vinyl and olefin

	1,2-Vinyl 1,2-PB	Olefin 1,4-PB
Enthalpy ΔH°	-30.3kcal/mol ⁻¹	-27.6kcal/mol ⁻¹

The higher reactivity of 1,4 olefin can be also explained from the difference in enthalpy (Table 4)⁽⁸⁾.

3. Example of rubber modification by crosslinking

3.1 EPDM modification

Table 5 shows an example of EPDM rubber modification using polybutadiene. Table 6 shows the effect of this modification.

Table 5. Example of EPDM modified with 1,2-polybutadiene

Material name	Phr
EPDM ¹⁾	100
1,2-Polybutadiene	0,10,15,30
Zinc oxide	5
Stearic acid	1
Calcined clay	120
Carbon black	5
Paraffinic oil	6
Paraffin wax	5
Dicumyl peroxide (DCP)	7
Dibenzoylquinone dioxime	1.5

1) Ethylene content: 42%, ENB content: 0.7%, ML1+4 (125°C): 27

Preparation method of EPDM/polybutadiene combination

All raw materials, including polybutadiene, were mixed and kneaded with a Banbury mixer (filling rate 70%, 23°C, 50 rpm). Banbury mixer B600, Toyo Seiki Co., Ltd.

A cross-linking product was prepared from the EPDM/polybutadiene combination, and a test piece (dumbbell No.3, large) was created.

Press condition: 170 ± 1°C × 10–15 min,

Electric heating press: Otake Kikai Kogyo Co., Ltd.

All evaluations were performed according to the ISO standard. The evaluation conditions are provided at the end of this document.

Table 6. Mechanical properties of EPDM with 1,2-Polybutadiene

1,2-Polybutadiene 1,2-Vinyl content :92% (m/n=92/8) M _n =3,200 (phr)	Mechanical Properties				
	Shore hardness	Tensile strength at break (MPa)	Elongation at break (%)	Modulus (MPa)	
				M100	M200
0	A63	5.33	620	2.24	3.00
15	A71	6.80	350	3.72	4.76
30	A78	6.95	250	4.91	6.30

Table 7. Oil resistance and compression set of EPDM with 1,2-Polybutadiene

1,2-Polybutadiene 1,2-Vinyl content :92% (m/n=92/8) M _n =3,200 (phr)	Oil resistance ¹⁾				Compression set ²⁾		
	Standard oil		Standard oil		23°C	60°C	100°C
	IRM901		IRM903				
	Δm (%)	ΔV (%)	Δm (%)	ΔV (%)	(%)		
0	49	76	129	190	16	18	20
15	36	54	93	134	13	13	12
30	33	48	86	120	18	16	15

1) Temperature: 70°C±2°C、72hours , 2) Compression ratio: 25%、72hours

When 1,2 polybutadiene (containing 92% of 1,2 vinyl group, M_n 3200) was added to EPDM at 15 phr and 30 phr, the rubber hardness, tensile strength, and modulus tend to increase according to the added amount. In contrast, elongation at break tends to decrease, which suggests that 1,2-vinyl groups of 1,2-polybutadiene are crosslinked in EPDM rubber. With regard to oil resistance, changes in both volume and weight are smaller than the added amount of 1,2-polybutadiene. It is presumed that the 1,2-vinyl group in 1,2-polybutadiene crosslinked in EPDM rubber and prevented oil ingress. The compression set is noteworthy. The addition of 1,2 polybutadiene further reduces the compression set and increases the elasticity (liquid tightness). EPDM rubber is excellent in terms of the compression set and is used to make seals and gaskets. The addition of 1,2 polybutadiene can increase the density of the seals and gaskets. However, it was suggested that this effect was not correlated with the amount of 1,2 polybutadiene added and that there was an appropriate value (15 phr. Table 5).

As stated above, we confirmed that there was a certain correlation between the amount of 1,2 polybutadiene added and the extent of crosslinking (hardening). Next, we discuss the relationship between the vinyl content in polybutadiene (Fig. 2, Ratio of m) and the outcome of the crosslinking (hardening) reaction at a fixed amount of polybutadiene (10 phr; Tables 8 and 9). The formulation to improve the quality of EPDM rubber was based on Table 2.

Table 8. Mechanical Properties of EPDM with Polybutadiene

Polybutadiene	phr	Mechanical properties				
		Shore hardness	Tensile strength at break (MPa)	Elongation at break (%)	Modulus (MPa)	
			(MPa)	(%)	M100	M200
Not added	0	A69	6.69	500	2.67	3.30
m/n = 22/78: M _n =2,500	10	A67	7.08	550	2.46	3.22
m/n = 48/52: M _n =2,100	10	A69	6.98	470	2.79	3.60
m/n = 66/34: M _n =2,500	10	A70	7.24	390	3.03	3.83
m/n = 92/8 : M _n =3,200	10	A71	7.42	380	3.15	3.95

Table 9. Oil resistance and compression set of EPDM with Polybutadiene

Polybutadiene	phr	Oil resistance ¹⁾				Compression set ²⁾		
		Standard oil		Standard oil		23°C	60°C	100°C
		IRM901		IRM903				
		Δm (%)	ΔV (%)	Δm (%)	ΔV (%)	(%)		
Not added	0	46	72	109	162	17	18	21
m/n = 22/78: $M_n=2,500$	10	46	70	110	160	17	20	20
m/n = 48/52: $M_n=2,100$	10	44	66	100	145	14	16	16
m/n = 66/34: $M_n=2,500$	10	41	63	92	134	13	15	16
m/n = 92/8 : $M_n=3,200$	10	38	58	89	130	12	15	17

1) Temperature: 70°C±2°C、72hours , 2) Compression ratio: 25%、72hours

When the content of the vinyl group (Fig. 2 Ratio of m) increases, the mechanical strength and oil resistance also increase. This is because the crosslinking density increases; mechanical strength and oil resistance are correlated with the crosslinking density, as is the case shown in Tables 6 and 7 (vinyl group content 92%, m = 92). The compression set is also correlated with the vinyl content, and the need for adding an appropriate amount, similar to that shown in Table 7, was not observed.

Increasing the amount of 1,2 polybutadiene (Tables 6 and 7) and the vinyl group content (Fig. 2, Ratio of m) (Tables 8 and 9) increases the crosslinking density, thereby improving the rubber quality.

3-2. H-NBR modification

Examples of modified compositions (Table 10) and physical properties (Table 11) of hydrogenated NBR (H-NBR) by 1,2-polybutadiene (containing 1, 2 vinyl group 90% M_n 2100) are provided.

Table 10. Example of H-NBR modified with 1,2-polybutadiene

Material name	phr
H-NBR ¹⁾	100
1,2-Polybutadiene (1,2-Vinyl content :92%, $M_n=3,200$)	0, 10, 20, 30
4,4'- (α,α -dimethylbenzyl)diphenylamine	1
Zinc salt of 2-mercaptobenzimidazole	1
Carbon black	50
1,3-bis-(t-butylperoxyisopropyl)benzene	8

1) Bound Acrylonitrile: 36.2%, Iodine value (mg/100mg): <7%, ML1+4 (100°C): 85

Preparation method of H-NBR/polybutadiene combination

A kneading: All raw materials, including polybutadiene, were mixed and kneaded using a Banbury mixer (filling rate 70%, 50°C, 50 rpm).

Banbury mixer B600, Toyo Seiki Co., Ltd.

B kneading: After 1,3-bis- (t-butylperoxy isopropyl) benzene was added, the contents were kneaded with a biaxial roll (50°C ± 10°C, 25 rpm).

φ6 × 16 (6 inch roll), Ikeda Kikai Kogyo Co., Ltd.

The crosslinking product was prepared from the H-NBR/polybutadiene combination product, and a test piece (dumbbell No. 3, large) was created.

Press condition: 170 ± 1°C × 20-30 min

Electric heating press: Otake Kikai Kogyo Co., Ltd.

All evaluations were performed according to the ISO standard. The evaluation conditions are provided at the end of this document.

Table 11. Properties of H-NBR with Polybutadiene

1,2-Polybutadiene (1,2-Vinyl content:90% Mn=2,100) (phr)	Shore hardness	Elongation at break (%)	Modulus (MPa)	Compression set (%) ¹⁾	Presence of ozone crack
			M100	100°C	96hr
0	A72	340	5.1	20	No cracks
10	A83	230	10.7	12	No cracks
20	A87	180	13.3	9	No cracks
30	A89	140	13.0	12	No cracks

1) Compression ratio: 25%、72hours

Similar to the modification of EPDM rubber, the rubber hardness and modulus tended to increase with the addition of 1,2-polybutadiene in the H-NBR modification. It was suggested that there was a proper value for compression set, similar to the modification of EPDM with 1,2 polybutadiene (Table 7) (addition of 20 phr has the lowest compression set). Notably, ozone-resistance was retained with the addition of 1,2 polybutadiene, and no cracks were observed even in the 96 h ozone-resistance test. H-NBR is a hydrogenated material, raising concerns that the addition of a modifier (1,2-polybutadiene) containing a vinyl group may cause cracks because of residual double bonds at the time of crosslinking . In addition to improving the mechanical strength and elasticity by crosslinking , the absence of cracks caused by ozone makes it possible to expand the use as a rubber modifier, or outdoor use as OA equipment, medical devices, etc. (Table 11).

Conclusion

In this paper, we described the crosslinking of an alkyl vinyl group. We explained the reactivity of the ethylene group in “Introduction of vinyl curing” and introduced a method for replacing the electron-withdrawing group and performing the crosslinking of the acryl group with radical initiators to compensate for the low reactivity of the ethylene group. However, because acrylic hardening (crosslinking) increased the polarity of the cure system, the scope of application to electronic materials with low dielectric strength and insulation were limited. In contrast, crosslinking materials with electron-donating groups, such as alkyl vinyl groups, are useful for electronic materials because of their low polarity. However, materials suitable for crosslinking and the respective curing methods are limited, and research is still ongoing. We have presented examples to explain the crosslinking of an acryl vinyl group herein. It is expected that the findings will be useful for crosslinking formulation and design.

Test methods

- Mooney viscosity (ISO 289-2)
Apparatus: Shimadzu SMV-300J
- Hardness (ISO 7619-1)
Apparatus: Durometer type A
- Tensile test (ISO 37)
Apparatus: Shimadzu Autograph EZ-LX 1 kN
Sample size: 2 mmT x 5 mmW x 20 mmL (dumbbell type), where L is a grip-to-grip distance
Drawing speed: 500 mm/min, Temperature: 23±1°C
- Tearing test (ISO 34-1)
Apparatus: Shimadzu Autograph EZ-LX 1 kN
Sample size: unnicked angle tear strength
Drawing speed: 500 mm/min
- Liquid resistance (ISO 1817)
Apparatus: Toyoseiki Test Tube Aging Tester
Sample size: 2 mmT×25 mmW×25 mmL
Test condition: 80±1°C×168hours
Test liquids: Pure water, 600 ppm chlorine water, 20 wt% HCl, 10 wt% HNO₃
- Compression set (ISO 815-1, ISO 815-2)
Apparatus: Ueshima Geer Aging Oven AG-1110
Compression ratio: 25%
Test condition: 100±1°C×70hours

Reference

- (1) D. L. Boger, *Modern Organic Synthesis*; TSRI Press, La Jolla, CA, 223 (1999).
- (2) S. R. Wilson, *Org. Reactions*, **43**, 93 (1993).; R.B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965). Frontier Orbitals and Reaction Paths, Kenichi. FUKUI, and Hiroshi. FUJIMOTO, Eds., *World Scientific*, 1997.
- (3) For example, Sigmatropic rearrangement: J. A. Berson, T. Miyashi, and G. Jones, *J. Am. Chem. Soc.*, **96**, 3468 (1974). Cope rearrangement: C. Cope and E. M. Hardy, *J. Am. Chem. Soc.*, **97**, 4765 (1975).
- (4) Masakazu. HASHIMOTO, Teiji. KOHARA, and Yoshio. NATSUUME, JP05239123 Publication.
- (5) For example, using alkylate metal: Seiich NAKAHAMA and Akira HIRAO *Journal of Synthetic Organic Chemistry, Japan*, **44**, 137 (1986).
- (6) Hiroki HASHIMOTO, *Denzai Journal*, **637**, 14-17 (2018)., Hiroki HASHIMOTO, *Gijyutsujouhoukaishi*, Chapter 3, Section 16, 339-345, published (2021)., Hiroki HASHIMOTO ., *International Elastomer Conference*, ISSN: 1547-1977 , C20 (2021).
- (7) Yasunori. MATSUI, Kazuhiko. MIZUNO, and Hiroshi. IKEDA, *Journal of Synthetic Organic Chemistry, Japan*, **70**, 434 (2012).
- (8) Hiroki HASHIMOTO, Hiroshi SAKAI and Izumi TANDO, *Denzai Journal*, **646**, 25-31 (2020).
- (9) Hiroki HASHIMOTO, *European Rubber Journal*, Jan. (2019)., Hiroki HASHIMOTO, *Denzai Journal*, **640**, 8-11 (2019)., Hiroki HASHIMOTO *et. al.*, *International Elastomer Conference*, ISSN: 1547-1977, E20 (2019)., Hiroki HASHIMOTO, Hiroshi SAKAI and Izumi TANDO, *Journal of the Society of Rubber Science and Technology*, **93**, 273-278 (2020), Hiroki HASHIMOTO, *European Rubber Journal*, Sep. (2020).
- (10) Yasumasa. WATANABE, H. ISHIGAKI, H. OKADA and S. SUYAMA, *Polym. J.*, **29**, 366 (1997)., Yasutake HARA, Hidetsugu NAKAMURA, Takanori JINNOUCHI and Mamoru SHIMIZU, *Kogyo Kagaku*, Vol.52, No.5, 350-355 (1991)., MOF Corporation HP, http://www.nof.co.jp/upload_public/kobetsu/1010F020010.pdf



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