

Naturally Occurring Amino Acid: Novel Curatives for Chloroprene Rubber

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ABSTRACT: Polychloroprene is a diene rubber, but unlike other diene rubbers, its compounding with various additives and curing mechanisms is different. A derivative of thiourea, ethylene thiourea (ETU), is widely used to vulcanize chloroprene rubber (CR), and the vulcanizates thus obtained exhibit excellent mechanical properties, good aging resistance, and very good sealing properties. However, the problem is that ETU is reported to be a potent carcinogenic compound, and hence, the effective substitution for ETU has been extensively explored. In this study, we used a naturally occurring amino acid derivative, dimethyl L-cystine, as an ecofriendly com-

pound for the vulcanization of CR. It had a significant influence on the curing characteristics and mechanical properties, such as modulus, tensile strength, elongation at break, and hardness values. The concentration of this novel crosslinking agent and also the curing temperature were optimized. In the presence of dimethyl L-cystine, the amount and activity of magnesium oxide also exhibited significant influences on the crosslinking characteristics. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3981–3986, 2006

Key words: crosslinking; rubber; vulcanization

INTRODUCTION

Virginity is not a virtue in polymers. Most, if not all, of the man made polymers cannot be used in their virgin state. Therefore, for product application and to enhance polymer properties, a number of additives need to be mixed with rubber compounds. However, in the course of time, some portion of the additives will come out from the bulk to the surface and then to the atmosphere. Thus, the environment ultimately becomes contaminated if those additives are not ecofriendly. During past decades, chloroprene rubber (CR), one of the earliest synthetic elastomers, has proven its worth in many various technological applications.^{1–3} The vulcanization chemistry of CR is different from other diene rubbers.⁴ Generally, the vulcanization of CR compounds is carried out by the derivatives of thiourea, mainly ethylene thiourea (ETU), as curing agents or organic accelerators⁵ along with metal oxides. Although these vulcanizates offer excellent physical properties, good aging resistance, and very good sealing properties, the crosslinking agent, ETU, itself has

proven to be a potent carcinogenic compound.^{6–8} Therefore, the replacement of ETU by a safe accelerator is an urgent need today. Laws and regulation have already been issued in several countries to restrict the use of ETU. A number of efforts^{9–18} were made in the past to develop noncarcinogenic compounds as vulcanizing/crosslinking accelerators for CR. The aim of this investigation was to develop a safe accelerator that could replace ETU in its activity for vulcanizing CR. A derivative of a naturally occurring amino acid containing a disulfide linkage, dimethyl L-cystine, was successfully used as crosslinking agent for CR. Although the use of amino acids in different curable compositions have been reported,^{19–22} their use in curing CR has not yet been reported. The concentration of this novel crosslinking agent and the temperature of curing were optimized. The effect of dimethyl L-cystine on the curing characteristics and mechanical properties of the CR vulcanizate are critically discussed, and the results are compared with those obtained with ETU. This comparative study revealed that dimethyl L-cystine could be a replacement for ETU for vulcanizing CR. In the presence of dimethyl L-cystine, the amount and activity of magnesium oxide in the curing of CR was also studied. Because of the structural similarity of dimethyl L-cystine with hexamethylene diamine, a comparative study on the cure characteristics and physical properties was also carried out.

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TABLE I
Compounding Formulations of CR Vulcanizates at 160°C

	Mix no.										
	1	2	3	4	5	6	7	8	9	10	11
CR	100	100	100	100	100	100	100	100	100	100	100
Dimethyl L-cystine	9	0	0	9	0	0	6	12	9	9	9
ETU	0	9	0	0	9	0	0	0	0	0	0
Hexamethylene diamine	0	0	9	0	0	9	0	0	0	0	0
S	0	0	0	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MgO	4	4	4	4	4	4	4	4	0	2	6
R_{∞} (Nm)	6.9	7.9	7.8	8.9	8.0	7.8	7.7	8.8	6.2	6.9	7.8
t_2 (min)	1.5	1	0.5	2	1	0.5	1.5	1	0.75	1.5	2.5
t_{90} (min)	36	16	35	34	18.5	35.5	35.5	39	22	30	41

EXPERIMENTAL

Materials

The CR used in this study was xanthate disulfide type [Bayprene 215, Bayer, Leverkusen, Germany; ML 1+4 (at 100°C) = 50 ± 6, total ash content maximum = 1%, density = 1.23 g/cm³]. ZnO (Merck India, Mumbai), MgO (Merck India), stearic acid (Merck India), and resublimed sulfur (Merck India) were used in this study. ETU (technical grade) was purchased from a local market. Carbon black (N 550; Phillips Carbon Black, Durgapur, India) and the processing oil Elasto-710 (IOC, Faridabad, India) were used in this study. Iso-octane (2,2,4-trimethyl pentane, S. D. Fine Chemicals, Ltd., Kolkata, India) and toluene (Merck India) were used as received. L-Cystine (molecular weight = 240.30, C₆H₁₂N₂O₄S₂) was obtained from Merck.

Preparation of dimethyl L-cystine

Magnesium-dry methanol (200 mL) was put into a 500 mL round-bottom flask and placed in an ice bath. Thionyl chloride (20 mL) was added to this solution dropwise with continuous stirring. Then, 24 g of L-cystine was added to the mixture under stirring conditions. The round-bottom flask containing the reaction mixture was fitted with a calcium chloride guard tube, and the mixture was stirred for another 5 h after room temperature was attained. The liquid phase of the reaction mixture was removed on a rotary evaporator. Then, about 200 mL of diethyl ether was added to it, and the solid mass was precipitated. The solid mass was separated by the removal of the ether layer on a rotary evaporator. A saturated solution of sodium carbonate was added to the solid to raise the pH of the solution up to 8. Dimethyl ester of L-cystine was extracted with ethyl acetate three times. The ethyl acetate was dried with sodium sulfate (anhydrous) and concentrated on the rotary evaporator.

Preparation of the vulcanizates

Requisite amounts of MgO and stearic acid were incorporated sequentially in previously masticated rub-

ber on a Berstorff laboratory two-roll mixing mill (size = 203 × 102 mm; Berstorff, Hanover, Germany) with a 15-min compounding cycle. Finally, the accelerator, sulfur, and ZnO were added to the mix. The stocks were cured under pressure at 160°C to optimum cure. The mixing mill was cooled by water circulation during compounding.

Measurement of the physical properties

Physical properties, such as modulus, tensile strength, and elongation at break, of the vulcanizates were measured according to ASTM D 412-92 after 24 h of maturation of the same. The hardness was determined according to ASTM D 2240-85 with a Shore A durometer (Zwick & Co., Germany). In the aging experiment, the vulcanizates were aged for 72 h at 100 ± 1°C in a forced-air circulating oven. The aged specimens were then kept for a further period of 24 h at room temperature before the modulus, tensile strength, elongation at break, and hardness were measured.

RESULTS AND DISCUSSION

Curing characteristics

The compound formulation of CR with various additives is presented in Table I. The amount of additives such as ZnO, stearic acid, dimethyl L-cystine, ETU, hexamethylene diamine, MgO, and sulfur were used based on 100 g of rubber. Here, the conventional crosslinking agent ETU was used for the vulcanization of CR in a controlled stock. Hexamethylene diamine was used as a crosslinking agent to compare its effect with that of dimethyl L-cystine because these two compounds have close structural similarities (Fig. 1), with the only difference being the presence of a disulfidic linkage in the middle and two ester groups at the ends of the molecule of dimethyl L-cystine. To investigate the effect of sulfur, the vulcanization of CR in the presence of accelerators was carried out in the presence and absence of sulfur. As the vulcanization of CR with ETU⁴ is generally carried out at 160°C, in

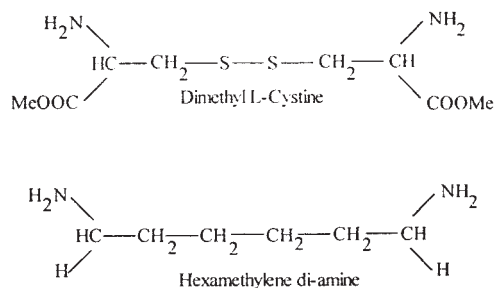


Figure 1 Chemical structure of dimethyl L-cystine and hexamethylene diamine.

this study, a vulcanization temperature of 160°C was also chosen.

As shown in Table I, among the sulfurless systems (mixes 1–3), the highest value for maximum rheometric torque (R_∞) was obtained for the ETU-containing formulation (mix 2). However, the scorch safety [scorch time (t_2)] for the stock containing dimethyl L-cystine (mix 1) was much better compared to that of the control formulation containing ETU (mix 2). However, the optimum cure time (t_{90}) was much higher when dimethyl L-cystine was used as crosslinking agent. We propose that dimethyl L-cystine acted as a difunctional crosslinking agent²³ like diamine for CR vulcanization. The proposed reactions are shown in Scheme 1.

Effect of sulfur

Mixes 4–6 (Table I) were used to envisage the effect of sulfur on the crosslinking of CR in the presence of the crosslinking agents under consideration. As shown in Figure 2 and Table I, sulfur promoted the crosslinking activity to a considerable extent because R_∞ was en-

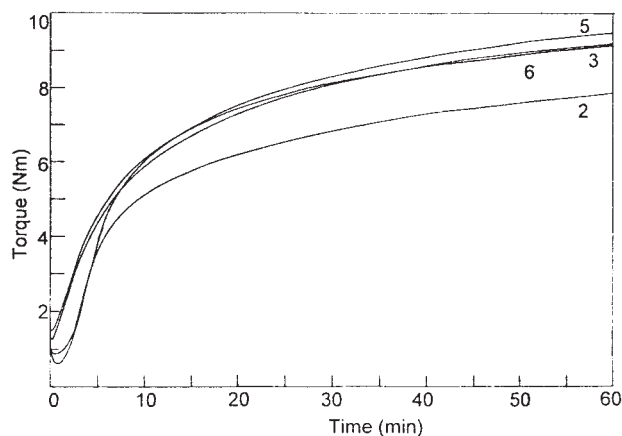
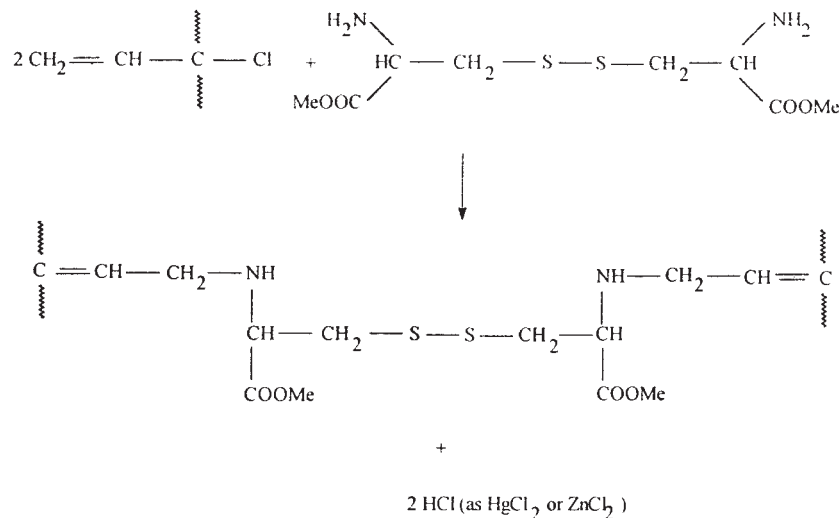


Figure 2 Rheographs of the mixes 1, 3, 4, and 6 cured at 160°C.

hanced to a great extent (cf. mixes 1 and 4). However, no such effect was observed when sulfur was used along with hexamethylene diamine (cf. mixes 2 and 5), a structurally symmetrical compound with dimethyl L-cystine. This revealed that the disulfide linkage present in dimethyl L-cystine also took part in the crosslinking of CR. When sulfur was used with ETU, no such activity was found (cf. mixes 2 and 5). During vulcanization, the temperature breaking of disulfide bond took place as the bond energy of the S—S bond decreased and a sulfur radical was formed. Again, it has been reported^{24,25} that during the crosslinking of CR in the presence of ZnO and MgO, diene, triene, and intramolecular cyclic structures are formed by dehydrohalogenation and molecular rearrangement. However, these diene and triene structures are supposed to provide crosslinking sites for sulfur vulcanization at the curing temperature.²⁶



Scheme 1

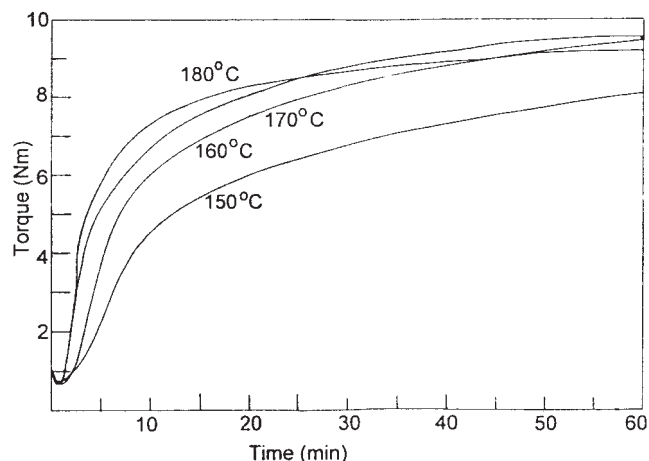


Figure 3 Rheographs of the CR compound (mix 4) at different temperatures.

Optimization of the dimethyl L-cystine concentration

To optimize the concentration of the dimethyl L-cystine mixes, the dosage of this compound was varied from 6 to 9 to 12 mM. The cure data (Table I) clearly indicates that R_{∞} was obtained when 9 mM dimethyl L-cystine (mix 4) was used; that is, at this concentration, the crosslinking density of the CR vulcanizate was at its maximum. At the same time, scorch safety (t_2) was higher, and t_{90} was shorter for 9 mM dimethyl L-cystine (mix 4). At a higher concentration (12 mM), the amino acid derivative seemed to form an amide linkage (see the Effect of Temperature section later) between one methyl ester group and the amine group of another molecule under the vulcanizing conditions, which resulted in a lower number of free amine groups, the effective reaction sites for the crosslinking reaction.

Effect of mgo

To investigate the influence of MgO on the vulcanization reaction of dimethyl L-cystine, the dosage of MgO was varied from 0 to 6 phr (mixes 4 and 9–11). As shown by the cure data in Table I, R_{∞} was obtained when 4-phr MgO was used. However, t_2 increased with increasing MgO concentration. t_{90} also increased increasing MgO proportion because MgO retarded the crosslinking reaction of CR in the presence of ZnO by scavenging hydrochloric acid.³ During vulcanization, HCl is formed in the rubber compound, and it reacts with ZnO to form $ZnCl_2$, which can act as a Lewis acid and accelerate the alkylation reaction of diamine crosslinking.⁴

Effect of temperature

To study the effect of temperature on the curing characteristics of CR with dimethyl L-cystine, mix 4, con-

taining 9 mM phr of dimethyl L-cystine, was vulcanized at four different temperatures: 150, 160, 170, and 180°C. The corresponding rheographs are depicted in Figure 3. The results (see Table II) clearly indicate that t_{90} and t_2 decreased with increasing temperature. R_{∞} increased with increasing temperature, attained its highest value at 160°C, and then diminished. The reason for the diminishment of R_{∞} beyond 160°C may have been due to the formation of amide linkages in dimethyl L-cystine at higher temperatures. To support the formation of amide linkages, dimethyl L-cystine was heated in xylene at 140°C, and the dried compound, before and after heating, was subjected to IR analyses. The analyses of the IR spectrum of the compound before heating [Fig. 4(a)] clearly indicated the presence of C=O stretching for ester at 1737 cm^{-1} , but the presence of both C=O stretching ester at 1732

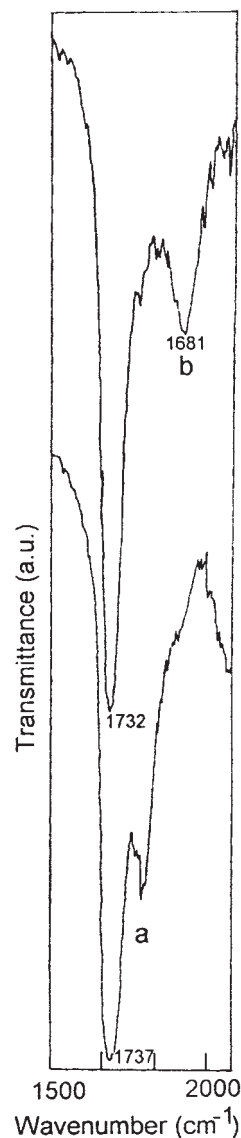


Figure 4 IR spectrum of dimethyl L-cystine (a) before and (b) after heating at 140°C.

TABLE II
Effect of Temperature on the Curing Characteristics of CR

	Temperature (°C)			
	150	160	170	180
R_{∞} (Nm)	73	88	88	85
t_2 (min)	2.15	2.0	1.5	1.0
t_{90} (min)	40	34	23	20
Cure rate index (min ⁻¹)	2.64	3.12	4.65	5.26

cm⁻¹ and C=O stretching for amide at 1681 cm⁻¹ in the spectrum of the compound after heating [Fig. 4(b)] clearly supported the formation of a partial amide linkage at this temperature. This led us to conclude that at a higher temperature, dimethyl L-cystine may have undergone a polymerization reaction to form an amide linkage in the rubber matrix between two molecules of dimethyl L-cystine, which rendered a lower number of free NH₂ groups available for crosslinking.

Physical properties

The physical properties of the CR vulcanizates are given in Table III. Among the sulfurless systems, although the 200% modulus was higher for the ETU-containing vulcanizates (mix 2), the tensile strength and elongation at break values were much higher for the dimethyl L-cystine containing vulcanizate (mix 1). The hardness values followed the same trend as the modulus. The incorporation of a flexible chain, present in dimethyl L-cystine between the two crosslink sites of CR, during vulcanization rendered the polymeric matrix predominantly elastic. As a result, the dimethyl L-cystine containing vulcanizates showed higher elongation at break values compared to the ETU-containing vulcanizate. The physical properties of the vulcanizates derived from the three different crosslinking agents in the presence of sulfur are also included in Table II. From the results, it is clear that when only dimethyl L-cystine was used as a crosslinking agent in the absence of sulfur (mix 1), the vulcanizate showed a lower modulus and higher tensile values than the vulcanizate containing ETU (mix 2), but when sulfur was used, the modulus value was enhanced to a con-

siderable extent, and the tensile value decreased to a small extent. For the sulfur-cured systems, all of the properties of the dimethyl L-cystine containing vulcanizates were superior to or comparable to those obtained with the ETU-cured vulcanizates. The influence of various concentrations of dimethyl L-cystine (mixes 4, 7, and 8) on the mechanical properties of the CR vulcanizates was studied, and the results are given in Table II. The 200% modulus continuously increased with increasing concentration of dimethyl L-cystine, but the maximum tensile strength was obtained for a concentration of 9 mM. This was due to the fact that when a larger amount of crosslinking agent was used for vulcanization, the vulcanizates became brittle and could not transmit stress. Therefore, the elongation at break values decreased with increasing concentration of the crosslinking agent. The effect of MgO on the physical properties of the dimethyl L-cystine containing vulcanizates are given in Table II (mixes 4 and 9–11). It is evident from the data that with increasing concentration of MgO, the 200% modulus continuously increased, but the tensile strength increased up to 4 phr MgO and then decreased. This was likely due to the fact that a higher concentration of MgO promoted the rubber molecules to rearrange into a more intramolecular cyclic structure and reduced the active crosslinking sites.²³

Aging behavior

The aging performance of the CR vulcanizates are shown in Table IV. It is evident from the aging data that the 200% modulus values increased in the aging experiment, which indicated postcuring of the CR vulcanizates. It is evident from the aging data that the enhancement of the modulus values was more pronounced for the vulcanizate containing dimethyl L-cystine and sulfur (mix 4). This was likely due to the fact that on aging, this vulcanizate, containing polysulfidic crosslinks, offered a monosulfidic linkage at the cost of polysulfidic linkages, which resulted in a larger enhancement of the modulus values. In mixes 4 and 9–11, various amounts of MgO were used, and it is evident from the results that with increasing MgO dosage, the retention of the physical properties in-

TABLE III
Mechanical Properties of CR Vulcanizates at 160°C

	Mix no.										
	1	2	3	4	5	6	7	8	9	10	11
200% modulus (Mpa)	1.55	1.73	—	1.78	1.77	—	1.65	1.80	1.38	1.53	1.91
Tensile strength (Mpa)	7.12	2.84	3.84	6.62	2.65	2.77	5.79	5.62	5.82	6.13	4.71
Elongation at break (%)	550	355	180	450	275	190	490	420	500	490	375
Hardness (Shore A)	50	58	55	58	59	56	53	53	54	56	59

TABLE IV
Aging Characteristics of the CR Vulcanizates at $100 \pm 2^\circ\text{C}$

Change in	Mix no.										
	1	2	3	4	5	6	7	8	9	10	11
200% modulus (%)	26	4	—	69	33	—	46	—	15	32	41
Tensile strength (%)	-54	-12	-10	-42	-52	-2	-50	-46	-51	-39	8
Elongation at break (%)	-54	-35	-7	-51	-23	-10	-58	-60	-42	-51	-46
Change in hardness (Points)	7	2	9	4	3	6	7	9	2	3	4

creased. It was reported that higher amounts of MgO are not desirable for the formulation of CR because this causes the formation of active double bonds, which are very susceptible to atmospheric oxygen, and causes undesirable aging effects.²³ However, we reported in an earlier publication²⁶ that the diene and triene structures that are formed in the presence of MgO participate in the sulfur crosslinking reaction accelerated by thiophosphoryl disulfide and ultimately enhance the tensile properties of the CR vulcanizate. Therefore, those diene and triene structures are no longer available for oxidation during prolonged aging. With higher amounts of MgO, more diene and triene structures are formed, and these are very much prone to oxidative degradation.

CONCLUSIONS

This study revealed that dimethyl L-cystine, a derivative of a naturally occurring amino acid, can be effectively used as a vulcanizing/crosslinking agent for poly(chloroprene rubber) and as a promising substitute for ETU. What is even more encouraging is that when this compound was used along with sulfur as an accelerator, superior curing characteristics and physical properties of the CR vulcanizates were achieved. However, a detailed study will be needed to reveal the chemistry behind this.

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