ORIGINAL ARTICLE

A direct method for the vulcanization of acrylate rubber through *in situ* coordination crosslinking

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In this work, a straightforward method of vulcanizing acrylate rubber (AR) was explored via the introduction of *in situ* coordination crosslinking. An inorganic metal salt, copper sulfate (CuSO_4), was mechanically mixed with AR and heat pressed to prepare a novel crosslinkable AR/ CuSO_4 composite. The determination of the coordination bonding between the ester groups of AR and copper (II) ions was performed with Fourier transform infrared spectroscopy based on the red shifts of the ester group absorption bands and the disappearance of the coordinated sulfate absorption bands, as well as by electron spin resonance based on the changes in the g-factor of copper (II). The crosslinking procedure of the composite was investigated through dynamic mechanical analysis. In addition, the extent of the crosslinking of the AR/ CuSO_4 composites was evaluated by observing the swelling behaviors. Scanning electron microscopy was used to investigate the morphology of the composite. The vulcanizates exhibited improved physical properties with high elongation at break due to exchange reaction between the ester groups of AR and CuSO_4 .

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INTRODUCTION

Acrylate rubbers (AR) exhibit the favorable qualities of weatherability, high temperature serviceability and good oil resistance. These qualities make the rubbers useful for under-the-hood automotive applications and outdoor applications. However, because AR is a saturated rubber, it is impossible for it to be vulcanized through traditional sulfur-vulcanizing systems like unsaturated rubbers. A considerable amount of research has been accomplished in the past years to introduce various types of active cure-site monomers into AR chains during the polymerization process. The most common cure-site monomers include those containing a labile halogen atom, a carboxyl group, an epoxide moiety, an unsaturated double bond, and a combination of two or more monomers resulting in dual or multiple cure sites, which require different curing systems as shown in Table 1. Despite significant advances in cure technology, all of the current acrylic elastomers require a relatively long cure cycle or must be post-cured.

In this work, we aimed to develop a straightforward method to vulcanize AR by introducing coordination-bond crosslinking. Ester carbonyl is capable of coordinating with metal ions, especially in solution systems. Metal complexes with carboxylic esters as ligands have long been in practice. A brief overview of low-molecular-weight organic compound complexes that contain coordinated ester groups was presented by Schreiner *et al.*²⁰ Multidentate ligands containing esters and other functional groups have been recently attracting the

attention of researchers because of their various coordination modes that are controlled by the subtle interplay between stereo-electronic factors. Attempts^{21–24} at such studies also revealed the coordination behaviors involving both the carbonylic and the alkoxy atoms of esters with metal ions. Moreover, regarding ester-containing polymers, Rolker *et al.*²⁵ observed that their viscosity was increased when they were treated with iron, cobalt or nickel carbonyl complexes at elevated temperatures in nitrogen. Nunnery *et al.*²⁶ considered this phenomenon and suggested the formation of a weak metal-COOR bond, where the inorganic species serve as weakly bonded bridges between the polymer chains, thereby promoting a rise in viscosity. Accordingly, ARs are prospective ligands for forming coordination crosslink structures upon the coordination of the polar ester lateral groups with metal ions. To our knowledge, however, there is little information available in the literature about the vulcanization of AR through coordination crosslinking. In this work, copper sulfate (CuSO_4) was used as a curing ingredient to vulcanize AR by a simple two-step process, including milling and heat press. It is expected that the issue involving the avoidance of introducing cure-site monomers and optimizing the corresponding curing system, the long-time cure circle and the post-cure process will be resolved with our proposed method.

We preliminarily focused on the coordination reaction, structure and properties of an AR/ CuSO_4 composite in this paper. The coordination reaction between the ester lateral groups and the copper

(II) ions was investigated by Fourier transform-infrared spectrometry (FT-IR), ESR, and dynamic mechanical analysis (DMA). The extent of the crosslinking of the AR/CuSO₄ composites was measured with a swell equilibrium method. The morphology and the mechanical properties of the novel AR/CuSO₄ composite were investigated by an scanning electron microscope (SEM) and a tensile test.

EXPERIMENTAL PROCEDURE

Materials and preparation

The AR used in this work was supplied by Zeon Inc. (Kawasaki, Japan) under the trade name AR42w, which contains an epoxy cure site with a Mooney viscosity of 33.5. CuSO₄ was purchased from the Shanghai Zhenxin chemical reagent factory (Shanghai, China).

The blending of the AR and the CuSO₄ was implemented in an open two-roll mill at room temperature. After mixing, the compound was discharged and compression molded into 1-mm-thick plates at a series of temperatures, including 150, 180 and 210 °C, for 20 min.

Characterization

Infrared spectra were obtained using a Bruker EQUINOX55 Fourier transform infrared spectrometer. The scanned wave number ranged from 4000 cm⁻¹ to 400 cm⁻¹. The spectral resolution was 2 cm⁻¹. The samples were pressed into a film in a heat press at elevated temperatures for 20 min and were then cooled to room temperature. The thickness of the film sample for the FT-IR measurement was approximately 20 μm.

The ESR spectra were obtained with an X-band (9.86 GHz) ESR spectrometer (Bruker Biospin GMBH, Rheinstetten, Germany, Type EMX-8/2.7) at room temperature. The AR/CuSO₄ composite was ground to pellets before testing.

DMA was performed with a UBM Rheoel E4000 dynamic mechanical analyzer. Samples were cold pressed until flat and cut into small, thin sheets of 4 × 4 × 1 mm³ for DMA testing. In the non-isothermal experiment, the test temperature ranged from -30 to 300 °C. The heating rate of the temperature scan was 3 °C per min. In the isothermal experiment, the samples were tested

for 100 min at setting temperatures. The average strain was 0.05% at a frequency of 11 Hz.

The extent of the crosslinking of the heat-pressed AR/CuSO₄ samples was evaluated by their swelling behaviors using ethyl acetate as a solvent at room temperature for an immersion period of 8 days. Each sample was cut into a size of 10 × 10 × 1 mm³ in advance. The swelling index of the samples was calculated by the following equation:

$$Q = \frac{M_t - M_0}{M_0}$$

where Q is the swelling index of the sample, M_0 is the mass of the initial sample, and M_t is the mass of the swollen sample.

Tensile tests were carried out in a Shimadzu AG-2000A (Shimadzu, Tokyo, Japan) at room temperature with a grip separation rate of 200 mm per min using dumbbell specimens with 1 mm thicknesses.

The morphologies of the fractured surfaces of the samples were examined on a JEOL JSM-6360 SEM (JEOL, Tokyo, Japan). The samples were fractured before hand in liquid nitrogen and coated with a thin layer of gold.

RESULTS AND DISCUSSION

Coordination-bonded networks

Figure 1 shows the FT-IR spectra of the CuSO₄, AR, and AR/CuSO₄ composites before and after heat pressing. The characteristic absorption peaks of the CuSO₄ powder appeared to be 1206 cm⁻¹, 1174 cm⁻¹, 1100 cm⁻¹ and 1047 cm⁻¹ ($\nu_3(\text{SO}_4)$), 992 cm⁻¹ ($\nu_1(\text{SO}_4)$), 776 cm⁻¹, 641 cm⁻¹ and 605 cm⁻¹ ($\nu_4(\text{SO}_4)$), and 472 cm⁻¹ ($\nu_2(\text{SO}_4)$) (ν_1 , ν_2 , ν_3 and ν_4 correspond to four types of normal vibrations of sulfate). This result indicated that sulfate acted as a typical bidentate ligand.²⁷ The absorption bands at 674 cm⁻¹, 630 cm⁻¹ and 595 cm⁻¹ can be attributed to the coordinated sulfate in the spectra of the AR/CuSO₄ composites before heat pressing, which nearly disappeared following the heat pressing. It can be inferred that, when blended with AR, the coordination structure of the CuSO₄ changed, and after heat pressing, the sulfate contributed insignificantly to the coordination.

AR featured a C=O stretching band ($\nu(\text{C}=\text{O})$) at 1735 cm⁻¹, an asymmetrical stretching mode ($\nu_a(\text{C}-\text{O}-\text{R})$) at 1254 cm⁻¹ and a symmetrical stretching mode ($\nu_s(\text{C}-\text{O}-\text{R})$) at 1163 cm⁻¹, in addition to an epoxide group stretching band at 857 cm⁻¹ and a symmetrical stretching band at 957 cm⁻¹. The epoxide groups of the AR/CuSO₄ composites before and after heat pressing had insignificantly changed compared with those of the AR. This finding indicated that no coordination reaction occurred between the epoxide groups and the copper ions. In contrast, the ester group absorption bands of AR/CuSO₄ after heat pressing indicated obvious red shifts (listed in Table 2). The decreased carbonyl stretching frequency has proven to be an easy and accurate diagnosis for the coordination of the ester

Table 1 Species of cure-site monomers and their corresponding curing systems of acrylate rubbers

Cure-site monomers	Curing systems
Halogen groups	Soap-sulfur or peroxide ^{1,2} Trithiocyanuric acid and calcium hydroxide ³ Aliphatic polyamines ⁴
Carboxyl groups	Quaternary ammonium salts ^{5,6} Hexamethylenediaminecarbamate and N,N'-diorthotolylguanidine coagent ⁷
Epoxide groups ⁸	Quaternary ammonium salts An isocyanuric acid and a quaternary ammonium salt ⁹ UV ¹⁰
Unsaturated double bonds ¹¹	Sulfur or peroxide
Carboxyl groups and chlorine groups ¹²	Quaternary ammonium salt ¹³ Hexamethylenediaminecarbamate ¹⁴ Non-alkali metal oxy compound and a quaternary ammonium salt, a tertiary amine or a guanidine ¹⁵ A combination of sodium stearate and a tetramethylthiuram disulfide or a Group IB, IIB, IVA, VA, and VIA metal compound ¹⁶
Carboxyl and epoxide groups	Quaternary ammonium salts ¹⁷ A guanidine compound and a diamine compound ¹⁸
Aliphatic diaminecarboxylate ¹⁹	Polyvalent amine

Figure 1 FT-IR spectra of CuSO₄ (a), AR (b), and AR/CuSO₄ composites before (c) and after (d) heat pressing. A full color version of this figure is available at *Polymer Journal* online.

groups. By examining the wave number shifts in the bands for $\nu(\text{C}=\text{O})$, $\nu_a(\text{C}-\text{O}-\text{R})$ and $\nu_s(\text{C}-\text{O}-\text{R})$, the nature of the complex formation between the metal cations and the ester groups can be determined. It has been recognized since 1958 that the coordination of one oxygen atom of the ester carbonyl group leads to a remarkable decrease in the carbonyl stretching frequency and to an increase in the frequency of the C-O-R vibration.²⁸ Hull *et al.*²⁹ demonstrated that the coordination of both of the oxygen atoms of the ester group caused a decrease in the characteristic frequencies for all three of the vibration bands of the ester. In this case, both of the oxygen atoms of the ester group participated in the coordination with the copper ions because all three of the absorption bands of the ester group shifted to low wave numbers.

X-band EPR spectroscopy was used to gain further insight into the coordination sphere of Cu^{2+} in the complexes with AR. The ESR spectra of the powdered CuSO_4 and the AR/ CuSO_4 composite (Figure 2) exhibited anisotropic spectra with intense broad signals and no hyperfine structure at room temperature.

The g -Tensor values have been determined with the Knüßl method.³⁰ The $g_{\parallel}$ value provides information about the types of donor atom complexes with copper (II) and the strength of their interactions.³¹ Regarding the oxygen atoms from the two ligands, the strength of the interaction between the atoms and the copper (II) ions decreased with decreasing $g_{\parallel}$ values in the following order: sulfate

> ester group of AR. Kivelson *et al.*³² reported a $g_{\parallel} < 2.3$ for a covalent character of the metal-ligand bond and > 2.3 for an ionic character. By applying this criterion, the ionic character of the $\text{Cu}^{2+}-\text{SO}_4^{2-}$ bond and the covalent character of the $\text{Cu}^{2+}-\text{COOR}$ bond in the complexes in this study can be predicted. Cu^{2+} preferred to form stable coordination bonds with $-\text{COOR}$ as opposed to SO_4^{2-} .

The swelling behaviors of the vulcanizates reflect their crosslinking property. The swelling behaviors of the AR/ CuSO_4 mixtures in a 6-month reserve and the hot-pressed AR/ CuSO_4 composites in ethyl acetate were observed at room temperature and are presented in Figure 3. Incidentally, fresh AR/ CuSO_4 mixtures were capable of being dissolved in ethyl acetate in a few hours. The swell index (Q) of each sample reached a maximum when its crosslinking network extended as far as possible. The Q values of the samples with very low crosslinking densities decreased gradually, whereas the samples with high crosslinking densities reached a swell equilibrium. These results were thought to be dependent on the interfacial interactions between the CuSO_4 particles and the polymer chains. As observed in Figure 3, an increase in the heat-pressed temperature or the CuSO_4 content may subsequently increase the crosslinking density of the AR/ CuSO_4 composites.

It can be concluded from the above results that, due to the electron-donating property of the guest (ester group) and the electron-receiving property of the host (CuSO_4), coordination interaction is established, and the linear rubber macromolecules are crosslinked into a three-dimensional network with CuSO_4 particles as crosslinking points. A schematic diagram of the coordination of the crosslinked AR/ CuSO_4 composites is shown in Figure 4.

Table 2 Characteristic IR absorptions (cm^{-1}) of the ester group of the AR and AR/ CuSO_4 composites before and after heat pressing

	$\nu(\text{C}=\text{O})$		$\nu_a(\text{C}-\text{O}-\text{R})$		$\nu_s(\text{C}-\text{O}-\text{R})$	
	Peak	Red-shift	Peak	Red-shift	Peak	Red-shift
Raw AR	1735		1254		1163	
AR/ CuSO_4 before heat pressing	1733	−2	1254		1160	−3
AR/ CuSO_4 after heat pressing	1727	−8	1242	−12	1158	−5

Abbreviations: AR, acrylate rubber; CuSO_4 copper sulfate; IR, infrared

Figure 2 ESR spectra of CuSO_4 and AR/ CuSO_4 composite after heat pressing.

Coordination crosslinking reaction of AR/ CuSO_4

DMA was used to investigate the coordination reaction in an AR/ CuSO_4 mixture. Figure 5 shows the variation in the storage modulus (G') with the temperatures for raw AR and an AR/ CuSO_4 mixture. AR has a suitable thermal stability. In the glass transition region (0 to 50 °C), the value of G' of the AR decreased monotonously. G' of the AR/ CuSO_4 mixture had the same decreasing tendency as it did in the beginning, whereas the degree to which it decreased became less (stage 1, Figure 5) in the temperature range from 25 to 50 °C. The reason for this trend was that (1) the motion of the AR chain segments was restricted by several of the coordination bonds between $-\text{COOR}$ and Cu^{2+} that were generated during milling and storage. The value of G'

Figure 3 Swelling behaviors of AR/ CuSO_4 composites with CuSO_4 content of 5 phr, 10 phr and 20 phr in reserve for 6 months at room temperature (noted by RT-5, RT-10, and RT-20, respectively) and after heat pressing at 150, 180 and 210 °C for 20 min (noted by 150-5, 150-10, 150-20, 180-5, etc.). A full color version of this figure is available at *Polymer Journal* online.

Figure 4 Schematic representation of the coordination bonded AR/CuSO₄ networks. A full color version of this figure is available at *Polymer Journal* online.

Figure 5 Dynamic mechanical properties of raw AR and AR/CuSO₄ (100/10) mixture as a function of temperature. A full color version of this figure is available at *Polymer Journal* online.

of the AR/CuSO₄ mixture showed a downward trend (stage 2, Figure 5) and visible augmentation (stage 3); meanwhile, the value of G' of the AR decreased slowly with temperature. The downward trend in G' of the AR/CuSO₄ mixture was attributed to (2) the melting of the CuSO₄. The increasing trend (3) in G' was thought to be the result of the formation of three-dimensional networks. Generally, a compatible filler or an additive can result in stronger chain segment interactions in a polymer either *via* chemical reactions or through physical adsorption. In this case, the coordination crosslinking formed as a result of the $-\text{COOR} \rightarrow \text{Cu}^{2+}$ bonds according to FT-IR. When the heating temperature reached 200 °C, the value of G' of the AR/CuSO₄ mixture stopped increasing (stage 4). The reason for this finding lies in the following aspects: the CuSO₄ crystals melted, and the coordination reaction rate decreased with the concentration of unreacted COOR groups and Cu²⁺ ions.

It is known that the crosslinking behavior of rubber materials at a fixed temperature is important for the design and establishment of process conditions, such as temperature and time. Therefore, the crosslinking behavior of an AR/CuSO₄ compound under an

Figure 6 Dynamic mechanical properties of raw AR and AR/CuSO₄ (100/10) mixtures as a function of time during isothermal processes: raw AR at 180 °C (a); AR/CuSO₄ mixture at 150 °C (b), 180 °C (c) and 210 °C (d). A full color version of this figure is available at *Polymer Journal* online.

Figure 7 SEM images of AR/CuSO₄ (100/10) composites: (a, b) unheated; (c, d) after heat pressing at 150 °C; (e, f) after heat pressing at 180 °C; (g, h) after heat pressing at 210 °C.

isothermal process was investigated by DMA (Figure 6). It was found that the value of G' of the raw AR at 180 °C barely increased, whereas the value of G' of the AR/CuSO₄ compound obtained under designed temperatures increased significantly with the increase in time, and the

resulting G' values increased with the rise in testing temperature. In addition, the value of G' of the AR/CuSO₄ compounds presented two outcomes: the initial value of G' increased rapidly and then smoothly. The concentration of the unreacted copper ions and the ester groups of the AR was initially high. The coordination reaction continued to occur as long as they encountered each other. The value of G' increased remarkably with the rapid formation of coordination networks. The motion of the chain segments then became increasingly difficult as a result of the restriction from the coordination crosslinking, as well as the decrease in the concentration of the unreacted function groups and the metal ions. Therefore, the coordination reaction rates declined gradually, leading to the smooth increase in the value of G' . Furthermore, the optimal crosslinking time (T_{op}) under different temperatures could be determined by the differential curves. It was found that T_{op} was too long for 150 °C and was 31 min and 20 min, respectively, for 180 and 210 °C.

Micromorphology

The micromorphology of the cross section of the AR/CuSO₄ composites before and after heat pressing at different temperatures is shown in Figure 7. As observed in Figures 7a–d, small particles were embedded, whereas large particles were separated from the AR matrix. This phenomenon was attributed to the weak interactions between tAR and CuSO₄ before heat pressing and after heat pressing at low temperatures (150 °C). In Figure 7e, all of the CuSO₄ particles were fixed in the AR matrix and surrounded by actinomorphic drapes after heat pressing at 180 °C. On the surface of the CuSO₄ particle,

there was a thin sheet (approximately 500 nm in thickness) of AR, as shown in Figure 7f. This finding indicated that strong interactions between the CuSO₄ particles and the AR chains were obtained due to the coordination reaction during heat pressing. The AR chains were crosslinked with these CuSO₄ particles as junctions. Moreover, for actinomorphic drapes, each CuSO₄ particle was surrounded by a dark ring after heat pressing at 210 °C, as observed in Figures 7g and h. This dark ring likely originated from the thawing of water during crystallization. All of these particles were embedded in the AR matrix, which also indicated strong interactions and suitable compatibility.

Mechanical property

Figure 8 shows the tensile behaviors of AR/CuSO₄ composites with a CuSO₄ content of 5 phr (parts per hundreds of rubber), 10 phr and 20 phr obtained after heat pressing at various temperatures. The strain-stress behaviors can be divided into two categories according to their trends with large deformation: a slow increase and a fast increase. The strain-stress curves of the AR/CuSO₄ composites obtained after heat pressing at 150 °C had a slow-increase trend with increasing elongation. The tensile behaviors of the others were similar to traditional rubber, and the tensile strength rapidly increased with an increase in elongation. The adhesion strength at the interface determines the load transfer between the components. A strong interfacial bonding between the particles and the polymer matrix was critical for the effective stress transfer, leading to a high composite strength. When an external stress was applied, several AR chains were easily separated from the surfaces of the CuSO₄ particles, as shown in Figures 7a and b. These particles were incompetent as firm crosslinks due to their weak interactions with the AR. Following high-temperature heat pressing, the AR chains were coordination bonded to the surfaces of CuSO₄ particles. When an external stress was applied, the motion of AR chains was limited by the CuSO₄ particles as crosslinks developed and the load efficiently transferred between the AR chains and the CuSO₄ particles. The AR/CuSO₄ composites showed pronounced reinforcement.

Furthermore, the AR/CuSO₄ composites displayed superior tensile properties with very high elongation at break. Several samples (150 °C–10 min, 150 °C–20 min, 180 °C–5 min) did not break in the measuring range. It is known that the exchange reactions between metal ions and carboxylate groups are specific for carboxylated ionic thermoplastics, ionic blends and ionic elastomers during melting flow.³³ In our case, the high elongation at break was also presumably related to the exchange reaction between AR and Cu²⁺, as shown in Figure 9. When an external force was applied, the molecular chains between the crosslinks (CuSO₄ particles and physical entanglement) were gradually stretched tight. When the stress was too large, several

Figure 8 Strain-stress curves of AR/CuSO₄ composites with CuSO₄ content of 5 phr, 10 phr and 20 phr obtained after heat pressing at 150, 180 and 210 °C for 20 min. A full color version of this figure is available at *Polymer Journal* online.

Figure 9 Schematic representation of the exchange reaction between AR and CuSO₄ under external forces and a simplified mode of 'live crosslinks.' A full color version of this figure is available at *Polymer Journal* online.

of the crosslinks decrosslinked as a consequence of the coordination bond dissociation. However, because the coordination reaction between AR and CuSO₄ can be carried out at room temperature, the crosslinks were able to reform through an exchange reaction as if they were 'live'. These reformed crosslinks resumed their function of bearing high stress. In the center of Figure 9, a simplified mode of the 'live crosslinks' in an ideal status is shown; the crosslinks could slide along the polymer chain through an exchange reaction as a uniaxial tension was applied. The chain segments between these 'live crosslinks' would become longer unless no crosslinks were regenerated. Hence, the AR/CuSO₄ composites displayed superior deformation with a very high elongation at break. This characteristic is distinguishable from sulfur vulcanizates and ionomers.

CONCLUSIONS

With this work, we created a straightforward method to vulcanize AR through the coordination reactions between the ester groups of AR and CuSO₄. The AR/CuSO₄ coordinate composites were prepared by simple mechanical blending and heat pressing. The results of FT-IR, ESR, equilibrium swelling and DMA demonstrated that coordination-bonded networks formed in the AR/CuSO₄ composites. The coordination reaction was capable of occurring at room temperature and was accelerated by increasing the temperature. SEM images showed that the AR chains bonded to the surface of CuSO₄ in the AR/CuSO₄ composites. The extent of the crosslinking and the tensile properties of the AR/CuSO₄ composites increased with the CuSO₄ load and the heat pressing temperature, which was determined by their swelling behaviors and their tensile behaviors. The considerably high elongation at break was specific to the AR/CuSO₄ composites, which was presumably due to the exchange reactions between the ester groups of the AR and the copper ions.

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