

Microencapsulation of Sulfur in Poly(urea–formaldehyde)

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ABSTRACT: Poly(urea–formaldehyde) (PUF) microcapsules loaded with sulfur were prepared by *in situ* polymerization. Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), differential scanning calorimetry and thermogravimetric (TG) analysis were used for the characterization of the obtained microcapsules. The chemical structure of the microcapsules was determined by FTIR. SEM analysis showed that the microcapsules were spherical and that the mean diameter of microcapsules was $42 \pm 1 \mu\text{m}$. Thermal analysis showed that the microcapsules were thermally stable below 247°C. The release properties of sulfur from the PUF microcapsules during the vulcanization of acrylonitrile–butadiene

rubber (NBR) were studied by analysis of the vulcanization properties. The results show that at a vulcanizing temperature of 160°C, all of the sulfur entrapped in PUF was released out through the microcracks and pores of the shell, and the curing time of the microcapsule curing system compared with that of the sulfur curing system was longer. The mechanical properties of the NBR vulcanized by sulfur microcapsules were better than those of the NBR vulcanized by sulfur. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 767–773, 2011

Key words: core–shell polymers; microencapsulation; rubber; thermal properties; vulcanization

INTRODUCTION

Microencapsulation is described as a process of enclosing micrometer sized particles of solids or droplets of liquids or gasses in an inert shell. The shell is often made of thin synthetic or natural polymeric membranes. Through selection of core material and shell, it is possible to endow microcapsules with a variety of functions. Microencapsulation has potential extensive applications in the fields of flame retardants, pesticides, pharmaceutical and medical applications, foods, biology, self-healing materials, carbonless copying paper, and many other areas.^{1–5}

As is already known,⁶ two forms of sulfur are used as vulcanizing agents: soluble (rhombic crystals of S₈ rings) and insoluble (polymeric) sulfur. However, in the vulcanization process, soluble sulfur usually migrates to the surface of a rubber compound and crystallizes when large amounts of soluble sulfur are used. Insoluble sulfur is recognized as an excellent vulcanizing agent to prevent blooming because it disperses in rubber as discrete particles that cannot diffuse through the rubber. However, insoluble sulfur is much more expensive than soluble sulfur and

is easy to transform into soluble sulfur above 120°C. These disadvantages limit the application of the two forms of sulfur in the rubber industry.

Recently, to solve the problems mentioned previously, some researchers have devoted studies to encapsulating sulfur in polymeric materials to develop a novel vulcanizing agent. Monika and coworkers^{7,8} successfully prepared the microcapsules filled with sulfur by a physical mixing method in patents. The microcapsules can not only be used as a kind of vulcanizing agent but can also be used as a kind of self-healing material. Gobinath et al.⁹ processed the sulfur entrapped in polymeric materials with rubber polymers to provide a kind of self-healing material, which can be used to repair cracks in the inner position of a tire. To our best knowledge, this is the first article describing the microencapsulation of sulfur in poly(urea–formaldehyde) (PUF) by *in situ* polymerization. The PUF shell has nice thermal stability, which can prevent the release sulfur from microcapsules in the processing step of a rubber compound and prevent blooming. However, above a certain temperature, the shell wall softens or melts; this leads to the leakage of sulfur and crosslinking between sulfur and the rubber. In this study, the existence of PUF particles coated on sulfur surfaces was determined by Fourier transform infrared (FTIR) spectroscopy and examined under scanning electron microscopy (SEM). The thermal stability of the microcapsules was investigated by differential scanning calorimetry (DSC) and TG. The microcapsules were used as rubber additives, and the

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release properties of sulfur during the vulcanization of acrylonitrile–butadiene rubber (NBR) was studied by analysis of the vulcanizing properties.

EXPERIMENTAL

Materials

Sublimed sulfur was purchased from Tianjin Fuchen Chemical Reagent Co. (Tianjin China). Gelatin, a biochemical reagent, was provided by Tianjin Yingdaxigui Chemical Reagent Co. (China). Urea (U), an analytically pure agent, and formaldehyde (F), another analytically pure agent (37 wt %), were supplied by Tianjin Fuchen Chemical Reagent Co. Triethanolamine and formic acid, used for controlling the pH value of the solution, were provided by Beijing Chemical Works (China). Carbon disulfide was supplied by Tianjin Fuchen Chemical Reagent Co. NBR (220S) was provided by Japan Synthetic Rubber Co. Carbon black (N330) was supplied by Degussa (Germany). Stearic acid (1800) was purchased from Alxa Chemical CO. LTD (Jakarta Indonesia). Zinc oxide and the accelerator were purchased from Pan-Continental Chemical Co., Ltd.

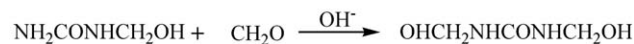
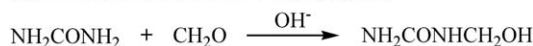
Microcapsule preparation

The microencapsulation of sulfur was carried out in a 250-mL, three-necked, round-bottom flask equipped with a mechanical stirrer via *in situ* polymerization. An F solution (20 mL, 37 wt %) was adjusted to pH 9 with a 10 wt % Na₂CO₃ solution in the 250-mL three-necked flask. After 10 g of U was added, a clear solution was formed at 70°C, and heating was continued for 1 h to prepare a prepolymer solution of U and F. Sulfur (10 g), deionized water (50 mL), sodium dodecyl sulfonate (SDS; 0.05 g), and a 10 wt % aqueous solution of gelatin (10 mL) were added to the aqueous solution of the U–F prepolymer. The mixture was vigorously dispersed by a homogenizer (FM200 Fluko) at a selected rate. The suspension was adjusted to pH 3 with a formic acid solution. The polymerization of U–F and microencapsulation was attained with continuous agitation for 1 h at 35°C. After that, the temperature was kept at 70°C for 2 h to cure the PUF microcapsules. Then, the pH of the solution was adjusted to 9 with a 10 wt % Na₂CO₃ solution to complete the reaction. After the suspension was cooled to 25°C and filtered, the microcapsules were washed with distilled water and dried in a vacuum oven. The synthesis of the PUF shell is shown in Figure 1.

Test of the core content of the microcapsules

The core content of microcapsules was determined by the extracting method.¹⁰ Sulfur entrapped in PUF was extracted by carbon disulfide after the micro-

(1) The reaction scheme of U-F prepolymer



(2) The reaction scheme of PUF

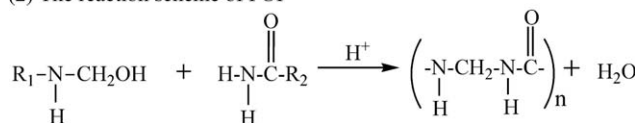


Figure 1 Scheme of the synthesis of PUF.

capsules were ground. The core content (W_{core}) of microcapsules could be calculated according to the following equation:

$$W_{\text{core}} = \frac{W_s - W_m}{W_s} \times 100\% \quad (1)$$

where W_s refers the weight of the original microcapsules and W_m refers the weight of the shell after sulfur has been extracted by carbon disulfide.

Characterization of the microcapsules

The surface morphology was monitored by SEM (Quanta 200F FEI). Samples were sputtered with a thin layer of gold–palladium to prevent charging under the electron beam. The microcapsule size and its distribution were determined with a scanning electron microscope equipped with image analysis software. The mean diameter of the microcapsules was obtained by the calculation of at least 250 microcapsules.^{11,12} The spectra of the microcapsules and pure PUF were recorded by FTIR (MAGNA-IR 560). The thermal properties of the microcapsules, sulfur, and PUF resin were analyzed by a differential scanning calorimeter (DSC 204 F4 Netzsch, Germany) under the protection of nitrogen flow at a heating rate of 10°C/min in the temperature range 20–800°C.

Use in the vulcanization of rubber

Sulfur or microcapsules, NBR, carbon black, zinc oxide, and accelerator were mixed by an open mill [X(S)L-160] and a curing press (XLB-O350 × 350, Huzhou Dongfang Machinery Co., Ltd., China). The curing formula is given in Table I. The amount of microcapsules (M_m) was calculated according to the following equation:

$$M_m = \frac{M_s}{W_{\text{core}}} \times 100\% \quad (2)$$

where M_s is the amount of sulfur and W_{core} is calculated according to eq. (1). In vulcanometry, several

TABLE I
Formulation of the Rubber Compound

Ingredient	Parts per hundred parts of rubber (phr)
NBR	100
Carbon black	45
Zinc oxide	5
Accelerator	1
Sulfur or microcapsules	5 or M_m

characteristic values of the curing process are determined according to a curometer (P3555B, Beijing Huanfeng Chemical Machine Co., Ltd., China). Examples are the minimum torque (M_L); the maximum torque (M_m); and the times for the modulus reach to $[M_L + (M_m - M_L) \times 10\%]$ (T_{10}), $[M_L + (M_m - M_L) \times 50\%]$ (T_{50}), and $[M_L + (M_m - M_L) \times 90\%]$ (T_{90}), respectively. T_{10} is called the *scorch time* and is a measure of the processing safety of a rubber compound. T_{90} is the optimal curing time. From the measured torque, the shear modulus (G) can also be calculated according to the following equation:

$$G = \frac{\tau}{\gamma} \quad (3)$$

where τ is the shear stress and γ is the strain. A universal testing machine (SANS) was used to test the Shore A hardness, tensile strength, elongation, 100% modulus, 200% modulus, and permanent deflection.

RESULTS AND DISCUSSION

Morphology and particle size of microcapsules

The surface morphologies and the size distribution of the microcapsules and sulfur were studied by SEM. Figure 2(a,b) shows that the sulfur particles presented irregular shapes and a smooth surface. The microcapsules shown in Figure 2(c,d), however, exhibited spherical shapes and a comparably rough surface with smaller particles scattered about, which appeared to be PUF microparticles. An SEM-energy dispersive X-ray analysis (EDAX) spectrum [Fig. 2(e)] recorded from a broken microcapsule revealed the presence of sulfur in the microcapsule. The rough surface suggests the coating of sulfur with PUF resin microspheres, and the PUF microcapsules with sulfur were observed to be larger than the sulfur particles. Figure 3 shows the mean diameter and the size distribution of sulfur and the PUF microcapsules. The mean diameters of the sulfur particles and

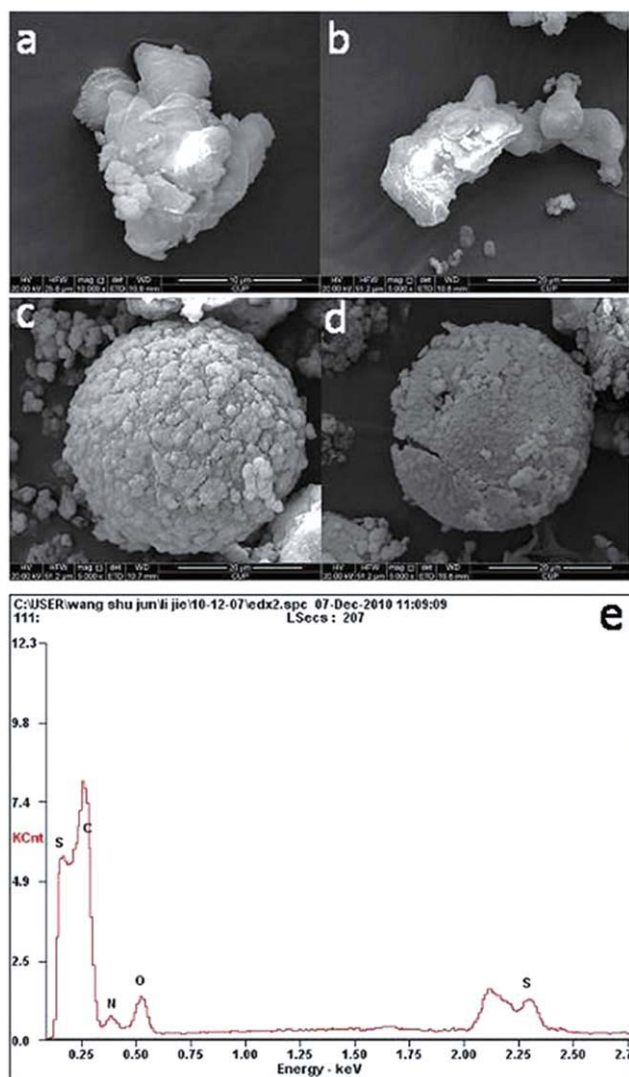


Figure 2 SEM images of the (a,b) sulfur and (c,d) microcapsules coating sulfur and (e) EDAX spectrum recorded from a broken microcapsule. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

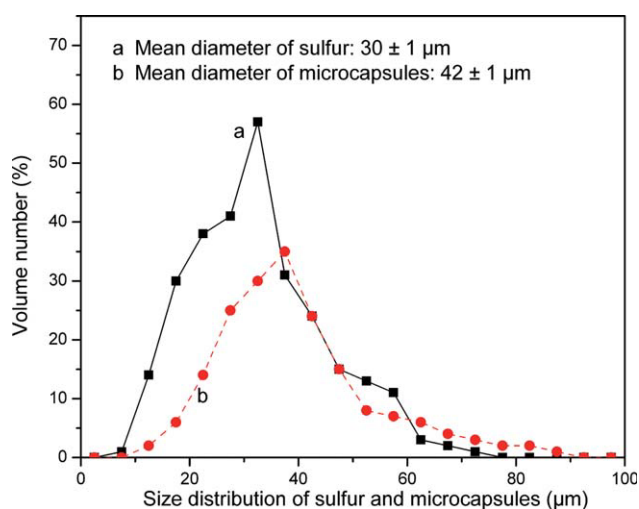


Figure 3 Particle size distribution of the (a) sulfur and (b) microcapsules. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

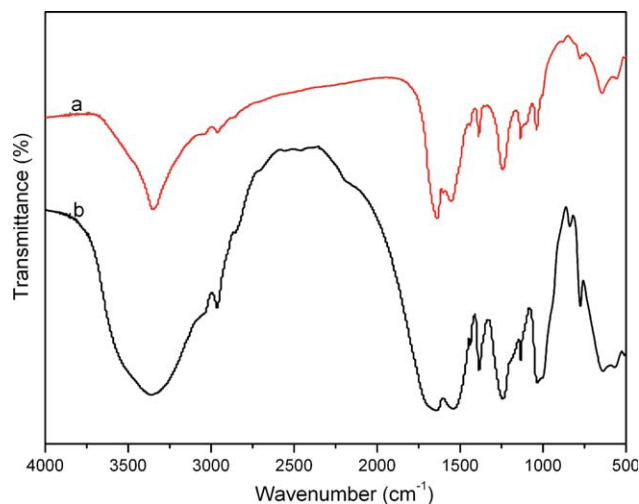


Figure 4 FTIR spectra of the (a) microcapsule and (b) pure PUF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

microcapsules were 30 ± 1 and 42 ± 1 μm , respectively. The size distribution of the microcapsules compared with that of sulfur was narrower.

FTIR of microcapsules

The FTIR spectra of the microcapsules and pure PUF resin are shown in Figure 4. A broad band at 3357 cm^{-1} attributed to O—H stretching and a strong absorption peak at 1638.16 cm^{-1} related to C=O stretching of an amide group could be seen in the spectrum of the microcapsules. Other characteristic peaks of an N—H stretching vibration at 1553.17 cm^{-1} , a C=O stretching vibration at 1638 cm^{-1} , a C—H stretching vibration at 1389 cm^{-1} , and a C—N stretching vibration at 1242 cm^{-1} are also shown. It can be seen that the FTIR spectrum of the microcapsules matched the spectrum of the pure PUF resin without a core; this confirmed that the shell was made of PUF resin.

Thermal analysis

Figure 5 shows DSC analyses of microcapsules, sulfur particles, and pure shells. In the curve of sulfur, the heat absorption peak at about 115°C was the melting point of sulfur, and the other heat absorption peaks at 105, 180, and 344°C corresponded to different phase transitions of sulfur. In the curve of pure PUF, the exothermic peak at 82°C was ascribed to the absorbed water. The strong exothermic peak at 250°C was attributed to the decomposition of PUF. Two strong endothermic peaks could be seen in the curve of the microcapsule. The exothermic peak observed at 115°C corresponded to the melting of sulfur that was encapsulated by PUF, which approached the melting point of sulfur. The other

strong exothermic peak at 247°C was attributed to the decomposition of the shell. It is noteworthy that the peak at 344°C in the curve of the core disappeared in the curve of microcapsules, whereas the peak at 115°C appeared. This phenomenon may be ascribed to the thermal interaction between the core material and the decomposition products of PUF at higher temperature. This was in an agreement with Yuan's¹³ work, in which thermally induced reaction might occur between the shell and core materials during decomposition. According to the DSC curve of microcapsules, showing the characteristic peak of the core material; the SEM-EDAX spectrum, revealing the existence of sulfur in the microcapsules; and FTIR, indicating that the shell was made of PUF, it can be well established that the microcapsules contained both sulfur and PUF.

The thermal characteristics of sulfur, PUF microcapsules of sulfur, and virgin PUF shells are illustrated in Figure 6. According to TG analysis, which presents residual weight (wt %) of the sample with increasing temperature, the weight of sulfur, PUF microcapsules of sulfur, and virgin PUF shells decreased with increasing temperature. In the curve of the core material, sulfur lost weight in one main step. About 94 wt % weight loss occurred between 255 and 350°C , corresponding to the evaporation of sulfur. The pyrolysis process of PUF can be subdivided into three stages.¹⁴ The first stage is a weight loss due to the adsorbed water ($<245^\circ\text{C}$). In the second stage, about 50 wt % loss of the total weight of the original sample occurs because of the fast thermal decomposition of PUF between 245 and 315°C . The last stage in PUF pyrolysis is a further cracking process of the residues in a wide

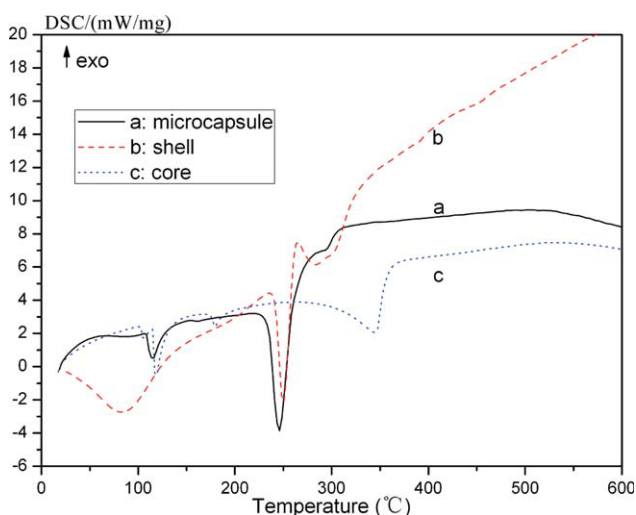


Figure 5 DSC curves of the PUF (a) walled microcapsules, (b) pure shell, and (c) sulfur. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

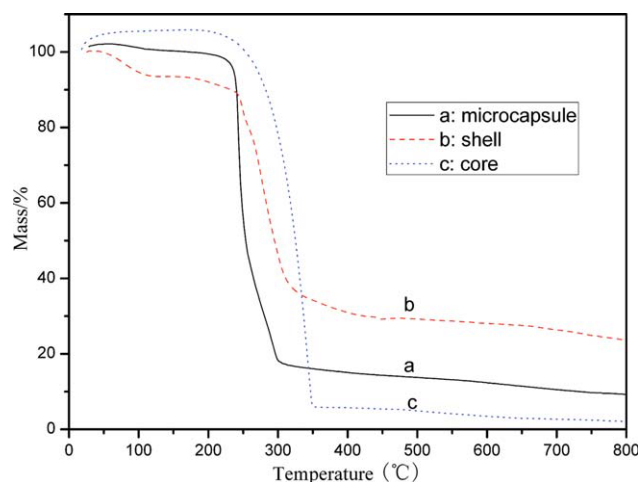


Figure 6 TG curves of the (a) PUF-walled microcapsules, (b) pure shell, and (c) core. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperature range, from 430°C to the end of this experiment (800°C). A total weight loss of 74 wt % was discovered at 800°C during pyrolysis. The degradation of the microcapsules could also be divided in three steps. In the first stage, the surface moisture and inherent moisture were emitted below 203°C. In the second stage, about 48 wt % of the total weight loss between 203 and 253°C and 32 wt % of the total weight loss occurred between 253 and 303°C. The results suggest that the degradation rate of microcapsules between 253 and 303°C was slower than that between 203 and 253°C. This phenomenon was explained by the fact that the weight loss between 203 and 253°C was due to the fast decomposition of large amounts of shells according to the pyrolysis of pure PUF resin, whereas the weight loss in the temperature range 253–303°C was attributed to the evaporation of sulfur released from the broken capsule shell and the decomposition of small amounts of residual shells. The last stage was the further cracking process of the residual PUF shells. About 10 wt % of the total weight loss occurred in this stage, and 91 wt % of the total weight loss was discovered at 800°C. The results indicate that sulfur could be released out through melting or softening of the shell above a certain temperature.

Release of sulfur during NBR vulcanization

According to the thermal analysis of the microcapsules, sulfur can be released out from the PUF microcapsules through breaking or softening of the PUF shell above a certain temperature. Thus, the prepared microcapsules seem to be suitable for use as vulcanizing agents. In this study, we used sulfur and microcapsules containing the same amounts of

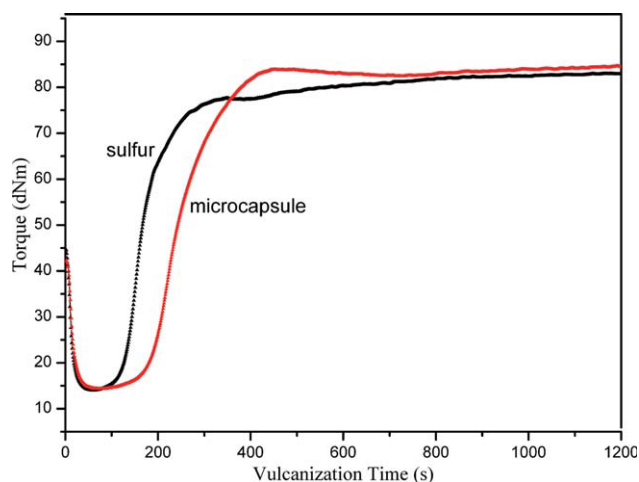


Figure 7 Vulcanization curves of the rubber vulcanized by (a) sulfur and (b) microcapsules (160°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sulfur [eq. (1)] as additives for the vulcanization of NBR at 160°C. The release properties of sulfur from the PUF microcapsules was studied by analysis of the vulcanizing properties.

The vulcanizing properties of the microcapsules and sulfur obtained from the vulcanization curves (Fig. 7) are listed in Table II. The scorch time (T_{10}) and the optimal curing time (T_{90}) of the microcapsule curing system were longer than that of the sulfur curing system. However, the torque difference ($M_m - M_L$) was found to have lesser variation from sulfur to the microcapsule curing system. This suggests that all of the sulfur entrapped in PUF was released out and crosslinked with rubber at 160°C. However, according to the DSC curve of PUF [Fig. 5(b)], the decomposition temperature of PUF was 247°C. Then, how was sulfur released out from the PUF microcapsules at 160°C? Previous work indicated that the polymer wall would commonly have a permeable part with a high porosity and a less permeable matrix part with a low porosity.¹⁵ It is believed that at 160°C, the PUF shells softened or broke; this generated microcracks and pores with bigger size, and then, the melted sulfur (mp = 115°C) diffused out through the microcracks and pores. It worth noting that the time differences between T_{50} and T_{10} in sulfur and the microcapsule curing system were 36 and 56 s, and the time

TABLE II
Vulcanizing Properties of Rubber Vulcanized by the Sulfur and Microcapsules

Vulcanizing agent	M_L (dNm)	M_m (dNm)	T_{10} (s)	T_{50} (s)	T_{90} (s)
Sulfur	13.98	82.95	129	165	293
Microcapsules	14.32	84.61	186	242	357

TABLE III
Mechanical Properties of Rubber Vulcanized by the Sulfur and Microcapsules Containing Sulfur

Vulcanizing agent	Vulcanizing time (min)	Shore A hardness (°)	Tensile strength (MPa)	Elongation (100%)	100% modulus (MPa)	300% modulus (MPa)	Permanent deflection (100%)
Sulfur	20	83	22.48	222.9	8.38	0.12	4
Microcapsules	20	86	26.79	307.5	6.16	26.73	4

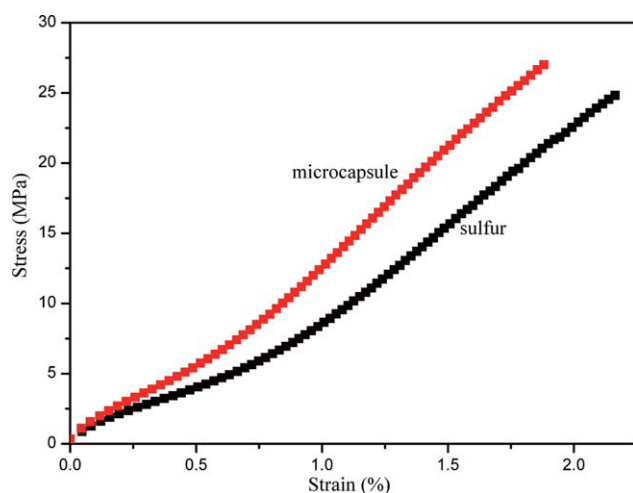


Figure 8 Stress–strain curves of the rubber vulcanized by sulfur and microcapsules. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

differences between T_{90} and T_{50} were 128 and 115 s, respectively. This indicates that the cure rate of the microcapsule curing system between T_{50} and T_{10} was slower than that of sulfur, whereas it was faster between T_{90} and T_{50} . This could be explained by the following reason. In the initial stage of vulcanization, the shell wall of the microcapsules was thermally stable and the release rate of sulfur was slow, and thus, free sulfur in the microcapsule curing

system was less than that in the sulfur curing system. As the vulcanization went on, the softening or breaking of the PUF shell was intensified for a long-time heat effect, resulting in a faster release of sulfur. Accordingly, the cure rate of the microcapsule curing system became faster. Tongjit et al.¹⁶ reported that microcapsule showed a quick response to temperature change to alter the release rate in a narrow temperature range. In our next work, the temperature range will be studied.

The mechanical properties of NBR vulcanized by sulfur and microcapsules are listed in Table III. It shows that at the same vulcanizing time, the shore A hardness, tensile strength, elongation, 100% modulus, and 300% modulus of the rubber vulcanized by microcapsules were better than those of the rubber vulcanized by sulfur. The stress–strain curves (Fig. 8) suggest that G of rubber vulcanized by the microcapsules was higher. All the results indicate that the rubber vulcanized by microcapsules containing sulfur had better mechanical properties than the rubber vulcanized by sulfur. This can be explained by the fact that the interfacial tension between NBR and PUF during melt mixing was low; this resulted in a mixture of polymer droplets of small size, and NBR, with a low critical entanglement spacing, drew the polymer of small size into finer fibers during the early phase of mixing and, accordingly, gave the higher quality blends with the polymer.¹⁷ Figure 9 shows the tensile fracture surface of rubber

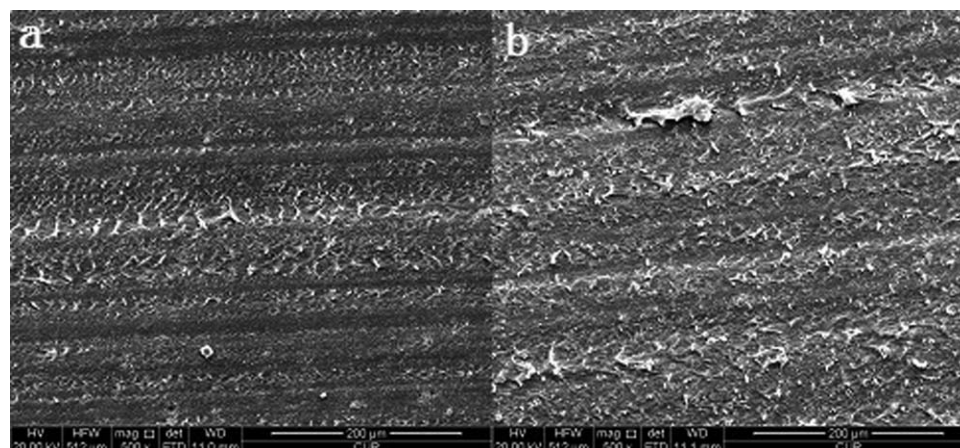


Figure 9 Tensile fracture surfaces of the rubber vulcanized by the (a) sulfur and (b) microcapsules.

vulcanized by sulfur and microcapsules. It exhibits that the tensile fracture surface of rubber vulcanized by the microcapsules was less smooth and indicated the dispersion of PUF in the rubber.

CONCLUSIONS

The PUF microcapsules filled with sulfur were successfully prepared by *in situ* polymerization. SEM showed that the obtained microcapsules were of spherical shape and the mean diameter was $42 \pm 1 \mu\text{m}$. Thermal analysis suggested that microcapsules were thermally stable below 247°C , and sulfur could be released from microcapsules above a certain temperature. The release properties of sulfur from the PUF microcapsules during the vulcanization of NBR was studied by analysis of the vulcanization properties. The results show that all of the sulfur encapsulated by PUF was released out, and the vulcanization of NBR was achieved at 160°C . However, the curing time of microcapsule-coated sulfur curing system was longer than that of the sulfur curing system because of the controlled release of sulfur. The mechanical properties of NBR vulcanized by microcapsules compared with that vulcanized by sulfur were improved by the reinforcing effect of the PUF shell.

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