리튬 아크릴레이트의 *In-situ* 중합을 이용한 수팽윤성 스티렌-부타디엔 고무의 제조

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Fabrication of a Novel Water Swellable Styrene-butadiene Rubber through the *In-situ* Polymerization of Lithium Acrylate

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Abstract: A novel water-swellable rubber (WSR) was prepared by blending styrene butadiene rubber (SBR) with dicumyl peroxide (DCP) and unsaturated carboxylic acid salt lithium acrylate (LiAA). The mechanical properties and water absorption behavior of WSR were studied. The results showed that LiAA was developed into polylithiumacrylate (PliAA) during the process of SBR vulcanization through *in-situ* polymerization, leading to the improvement of the mechanical properties and water absorption performance. The optimum usages of DCP and triallyl isocyanurate (TAIC) to attain the highest water swelling ratio for WSR were 3 and 1 phr, respectively. In addition, the tensile strength and the hardness of WSR were also enhanced by incorporating DCP or TAIC.

Keywords: water swellable rubber, *in-situ* polymerization, lithium acrylate, water absorption rate.

Introduction

The water swellable rubber (WSR) is a new type of polymer material, which possesses the unique characteristics of water-sealing in terms of water swelling and elastic sealing.[1-3] WSR is made of rubber matrix by introducing a hydrophilic group or a hydrophilic component. It can generate a great inflation pressure and its weight or volume will expand several times or even several hundred times after absorbing water.[4,5] Therefore, WSR can be used as a novel functional material to stop water by means of elastic sealing and swelling in water.

Generally, WSR can be prepared by incorporating Super Absorbent Polymer (SAP)[6] and unsaturated carboxylic acid salt.[7] The water absorbing mechanisms between SAP and the unsaturated carboxylic acid salt are different.[8,9] The hydrophilic groups of SAP are ionized into cations and anions in water, and meanwhile the anions are fastened to the SAP chain and the cations move freely into the mesh structure. There is a strong binding force between the hydrophilic groups and water molecules, so the water will permeate into the mesh structure of SAP to make it swell due to the osmotic pressure. On the contrast, the mechanism of the unsaturated carboxylic acid salt is that the acrylate develops into the polyacrylic acid salt during the vulcanization of rubber, and the polymerization of polyacrylic acid in the rubber matrix will lead to generate a new structure called interpenetrating polymer network (IPNs).[10] The water absorption effect of this WSR depends on the hydrophilic degree of the polyacrylic acid salt. Compared with adding SAP, the technology by making use of the interpenetrating polymer network through the *in-situ* polymerization of unsaturated carboxylic acid salt is more efficient because of the resultant IPN can present a finer dispersion and a more stable morphology.[11,12] Moreover, the water absorbing effect of polyacrylic acid salt is excellent. Therefore, the corresponded final properties of WSR by using the *in-situ* polymerization of

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unsaturated carboxylic acid salt will be greatly improved.

Rubber matrixes for fabricating WSR often contain natural rubber, nitrile rubber and polychloroprene.[13] However, the literatures about fabricating a water swellable rubber by using SBR matrix through the *in-situ* polymerization of lithium acrylate are still lacking.[7] Styrene-butadiene rubber (SBR) is a random copolymer prepared from the polymerization of butadiene and styrene monomer, and it has become the world's largest general-purposed synthetic rubber at present. According to the preparation method, SBR can be classified into emulsion polymerized butadiene styrene rubber (ESBR) and solution polymerized butadiene styrene rubber (SSBR).[14,15] SBR possesses outstanding physical properties, such as low dielectric constant, high abrasive resistance and good water resistance.[11] In addition, SBR can also be used as oil absorbing because of its crosslinking network structure. The water or oil swelling capability of SBR rubber can be enhanced by introducing hydrophilic groups or hydrophilic components. The large production of SBR makes it very attractive for fabricating WSR material.

In this research, SBR and DCP was used as the rubber matrix and curing agent, and the unsaturated carboxylic acid salt (LiAA) was added as the water absorbing component. The mechanical properties, water-swelling behavior of modified SBR will be investigated in this study. Our work will provide a novel fabrication method to obtain functionalized SBR with high absorption rate and extend their applications in this related area.

Experimental

Materials. SBR (1502) was supplied by Lanzhou Chemical Industry Corporation, Gansu Province, China. Lithium hydroxide (LiOH) was provided by Chongqing Jiecheng Chemical Company Limited. Acrylic acid (AA) was obtained from Wuhan Aladdin reagent Corporation. Dicumyl peroxide (DCP) was obtained from Shanghai Experiment Reagent Corporation. Triallyl isocyanurate (TAIC) was purchased from Qingdao Wan Lisheng Rubber Chemical Company Limited.

Preparation of Lithium Acrylate. Certain weight of LiOH was put into a beaker and place into an ice water bath. Afterwards, an appropriate amount of AA was slowly dripped in with continue stirring for half an hour. Then the product was collected and dried at 40 °C under vacuum.

Preparation of WSR. The neat SBR was plasticated on an open mill for 2 min at room temperature and then LiAA, zinc oxide, stearic acid and the other additives were fed into the two rollers in a certain order for mixing. Rubber compound slice was obtained from the open mill. After 24 h, it was placed into a $160 \times 120 \times 2$ mm^3 mould, preheated for 3 min and then vulcanized by compression molding for 15 min at 170 °C in a 10 MPa press.

Measurement and Characterization. Infrared (IR) spectra of the pure SBR, the mixture of SBR/LiAA, the vulcanized rubber of SBR/LiAA were recorded on a Nicolet Magna-IR750 Fourier transform IR (FTIR) spectrometer.

Tensile strength and elongation at break testing of standard dumbbell specimens were performed at room temperature with a crosshead speeds of 500 mm·min^{-1} by using a WDW-20 electronic universal tester (Shenzhen Kaiqiangli Testing Instruments, China). Hardness data was obtained from Shore hardness tester. Each test was carried out with six specimens for each sample and the averaged value was obtained.

The specimen dimension for the water swelling experiment was about $10 \times 10 \times 2$ mm. After accurately weighing, the sample was immersed in an excessive prepared solution, and taken out for weighing every time once in a while. Residual liquid on the sample surface was quickly soaked up by using the test paper before weighing. The water swelling ratio S was calculated by the following eq. (1):

$$S = \frac{m_2 - m_1}{m_1} \times 100\% \tag{1}$$

where m_1 and m_2 are the weights of the unswollen and swollen samples, respectively.

The sample dimension for the mass loss rate experiment is also about $10 \times 10 \times 2$ mm. The samples were immersed in an excessive tap water at room temperature after weighing and it soaked up to the equilibrium. Then, the samples were dried at 80 °C under vacuum till to a constant weight. The mass loss rate Q of WSR was calculated by the following eq. (2):

$$Q = \frac{m_1 - m_3}{m_1} \times 100\% \tag{2}$$

Where m_3 is the mass of the dried sample, which had been swelled with water. The mass of dried sample after swelled with water will decrease because of the separation of some hydrophilic components of WSR in water.

Scanning electron microscopy of WSR was performed on a Hitachi S-530 SEM machine. Samples were first cryogenically fractured in liquid nitrogen, mounted on a sample holder, gold sputtered and finally observed under the microscope.

Results and Discussion

Analysis of FTIR Spectra. The FTIR spectra of the pure SBR (curve a), the SBR/LiAA (curve b) mixture and the vulcanized SBR/LiAA (curve c) rubber are shown in Figure 1. All three spectra exhibited several characteristic absorbing peaks, including the peaks at 3000~3100 cm^{-1} corresponding to C-H stretching vibration on the benzene ring, the benzene skeleton vibration at 1600 and 1592 cm^{-1}, the in-plane blend vibration at 1440 cm^{-1}, the peaks at 967, 910 and 990 cm^{-1} assigned to the C-H bending vibration of trans-1,4-polybutadinene and 1,2-polybutadinene, the out-of-plane for C-H bending vibration at 700 and 760 cm^{-1}. In addition, the peak at 1570 cm^{-1} in b and c curves is corresponded to the C=O stretching vibration of -COOH and COOLi. Compared with the un-reacted SBR/LiAA mixture, the intensity of the out-of-plane bending vibration of C-H for C=CH$_2$ near 970 cm^{-1} is obviously weakened, indicating the polymerization of LiAA in the curing process.
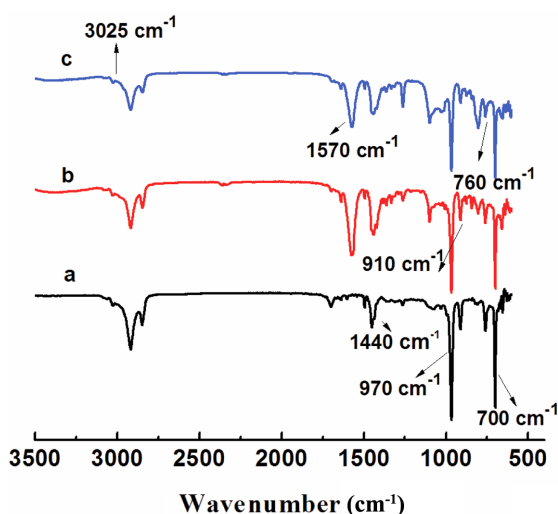

Figure 1. FTIR spectra of pure SBR (a); mixture of SBR/LiAA (b); vulcanized rubber of SBR/LiAA (c).

Mechanical Properties. The effect of the LiAA content on the mechanical properties of WSR is listed in Table 1. It can be clearly seen that the tensile strength and Shore hardness of WSR are increasing with LiAA content while the elongation at break of WSR is decreased. The *in-situ* polymerization of LiAA in SBR matrix can lead to the formation of IPN structure, which can introduce more physical crosslinking point to SBR, thus the tensile strength of SBR can be enhanced. However, the introduction of a new different polylithiumacrylate (PLiAA) phase will lead to the decrease of the elongation at break of SBR because of the phase separation. After absorbing water, the tensile strength and the elongation at break began to decrease. This phenomenon is obvious when the LiAA content exceeds 30 phr. The possible reason is that the crosslinking degree of WSR is increased after LiAA has developed into PLiAA though *in-situ* polymerization. Moreover, PLiAA plays a significant role in the water absorption of WSR. Water molecules are penetrated into the mesh structure of PLiAA during the process of water absorbing due to the osmotic pressure differences. Therefore, the mesh structure of WSR may be expanded or even destroyed, subsequently, the mechanical properties of the swelled rubber is declined.

The effect of the DCP content on the mechanical properties of WSR is presented in Table 2. It can be clearly seen in Table 2, the tensile strength and Shore hardness of WSR are increasing with DCP content while the elongation at break is decreased. When the content of DCP exceeds 3 phr, the mechanical properties of WSR start to change slowly. This is caused by the dual function of DCP in the curing process. DCP not only can be served as the crosslinking agent but also can be served as the initiator. When DCP is heated to a certain temperature, it will decompose to generate free radicals. These free radicals can seize the hydrogen of the SBR chain to be the macromolecular radicals, and then the coupling reaction between the chain radicals will form to chemical crosslink. In

Table 1. Influence of LiAA Content on the Mechanical Properties of WSR (in tap water)

LiAA (phr)	Shore hardness (HA)	Elongation at break (%)		Tensile strength (MPa)	
		Before absorbing	After absorbing	Before absorbing	After absorbing
10	43	122.3	98.5	3.8	2.5
20	46	120.8	107.5	4.2	3.3
30	48	117.3	98.1	5.3	3.4
40	49	112.4	95.6	5.7	2.7
50	51	110.7	78.3	5.9	1.2

Formula: SBR 100, SA 2, DCP 3, TAIC 2, LiAA variable, Soak temperature: 25 °C.

Table 2. Influence of DCP Content on the Mechanical Properties of WSR (in tap water)

DCP (phr)	Shore hardness (HA)	Elongation at break (%)	Tensile strength (MPa)
1	44	183.7	4.2
2	47	150.6	4.6
3	48	117.3	5.3
4	50	107.2	6.2
5	52	88.1	7.0

Formula: SBR 100, SA 2, LiAA 30, TAIC 2, DCP variable, Soak temperature: 25 °C.

Table 3. Influence of TAIC Content on the Mechanical Properties of WSR (in tap water)

TAIC (phr)	Shore hardness (HA)	Elongation at break (%)	Tensile strength (MPa)
0.5	47	89.2	4.9
1	48	117.3	5.3
1.5	48	123.21	5.7
2	49	127.7	6.2
2.5	51	133.5	6.5

Formula: SBR 100, SA 2, Li AA 30, DCP 3, TAIC variable, Soak temperature: 25 °C.

addition, some PLiAA may even can simultaneously graft to the rubber macromolecules in the process of the generation of PLiAA. In a word, the increase of the crosslinking density caused by DCP can lead to the improvement of the mechanical properties of WSR.

The effect of TAIC content on the mechanical properties of WSR is shown in Table 3. It is found that the tensile strength, the elongation at break and Shore hardness are all improved with the rise of the content of TAIC. The possible reason is that DCP and TAIC can form a bridge bond of the active agent during vulcanization. On the other hand, they can also prevent the macromolecule chains from breaking and the emergence of the disproportionation termination. Consequently, the degree of the crosslink of WSR is increased by the addition of DCP and TAIC. In addition, the extra crosslinking from the bridge bond of the active agent will lead to the enhancement of the mechanical properties. Therefore, TAIC in the curing system will promote the curing efficiency of DCP. The free radicals from TAIC can also initiate polymerization of LiAA, and even can be grafted to the double bond of SBR macromolecules to increase the crosslink degree. When the TAIC content is too high, the compatibility between TAIC and SBR will decrease

and the phase separation will emerge.

Water Absorption Behavior. The effect of the LiAA content on the water absorption behavior of WSR is shown in Figure 2. It shows that the water swelling ratio of WSR gradually increases with the LiAA content. However, the water swelling ratio of WSR achieves the maximum value when the content of LiAA is 30 phr. The reason is caused by the introduction of hydrophilic component of WSR; in other words, the introduction of PLiAA can increase the hydrophily of WSR. The cation and anion come from the disassociation of PLiAA in water. The anion is fasten to the rubber macromolecular chain and cannot move freely. However, the cation can move easily in the mesh structure, leading to the generation of osmotic pressure between the aqueous solution and the inside of WSR. Consequently, the water molecules will penetrate from the water phase to the inner mesh structure of WSR due to the effect of osmotic pressure. Thus both the water swelling ratio and the production of PLiAA will increase with the LiAA content. When the permeation stress of the water molecules was equal to the elastic stress of the covalent crosslink network of the WSR, the water-swelling ratio will reach to a maximum value.[7] The compatibility between PLiAA homopolymer and SBR will become worse when the PLiAA content is increased to a certain value. The PLiAA will also separate out from SBR matrix and will lead to the phase separation in the macro level. The mass loss of hydrophilic PLiAA from WSR will inevitably result in the decrease of the corresponding water swelling ratio.

The effect of the DCP content on the water absorption of WSR is shown in Figure 3. It can be seen that a maximum water swelling ratio appeared in this curve when the content of
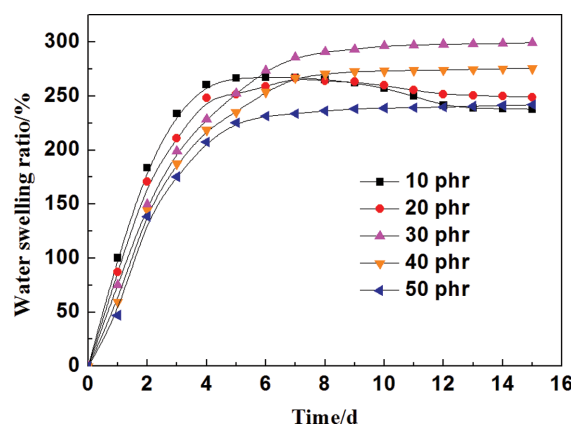

Figure 2. Influence of LiAA content on the water absorption of WSR (Soak temperature: 25 °C). Formula: SBR 100, SA 2, DCP 3, TAIC 2, LiAA variable.
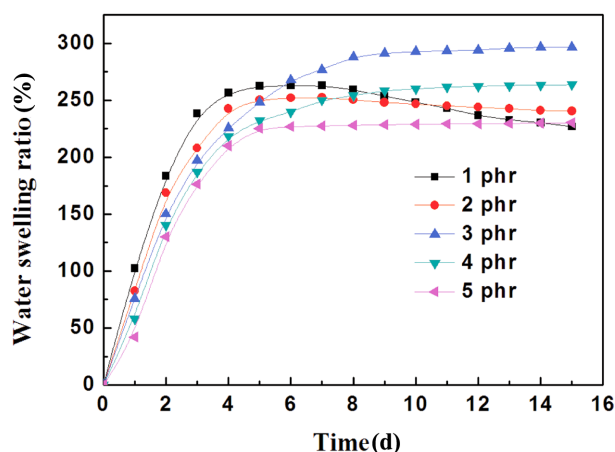
Figure 3. Influence of DCP content on the water absorption of WSR (Soak temperature: 25 ºC). Formula: SBR 100, SA 2, LiAA 30, TAIC 2, DCP variable.

DCP is 3 phr. When DCP is heated to a certain temperature, it will decompose to generate free radicals to initiate the polymerization of LiAA. PLiAA will generate and also graft to the rubber macromolecules in the meanwhile, leading to the increase in the crosslinking degree of WSR. However, the high crosslinking density is not good for the entrance of water to the meshes of WSR. Therefore, the optimum DCP content to obtain the maximum water swelling ratio is 3 phr.

The effect of TAIC content on the water absorption of WSR is shown in Figure 4. The water swelling ratio increases at first but later decreases with the amount of TAIC. There are two different reasons inside. On one hand, the free radicals resulted from TAIC can promote the curing efficiency of DCP. On the other hand, the polymerization and the grafting reaction will be
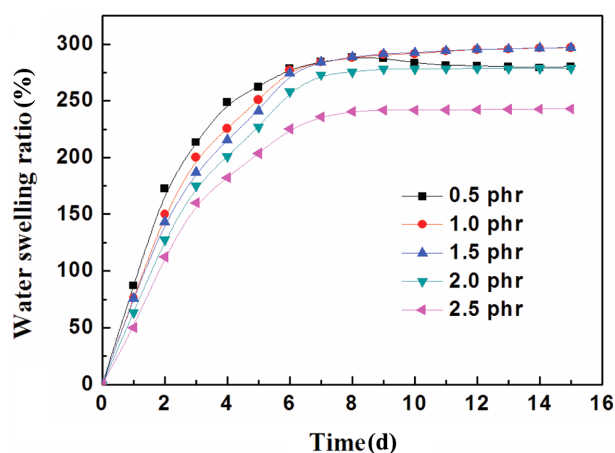
greatly improved by TAIC. When the content of TAIC is low, the loose mesh structure of WSR can lead to the precipitation of PLiAA. When the content of TAIC is high, the mesh structure becomes tight and complicated to reduce the physical crosslinking of PLiAA.

Mass Loss Rate of WSR. Though the water absorbing behavior of WSR can be improved by introducing the hydrophilic component, some part of LiAA or PLiAA homopolymer will separate from the WSR matrix and immigrate into water during the water swelling process. Therefore, the total weight of WSR after dried will decrease compared with that of the unswollen one. The mass loss rate can be used to indirectly illustrate the effect of different component on the structure stability of WSR after absorbing water.

The effect of LiAA content on the mass loss rate of WSR is shown in Figure 5. The mass loss rate of WSR is gradually increased with LiAA content after swelling. It is known that the hydrophilic PLiAA can increase the water swelling ratio of WSR. However, the introduction of hydrophilic PLiAA will also lead to the increase of mass loss ratio of WSR because of the bad compatibility between WSR and PLiAA. The increase of PLiAA will lead to the poor structure stability of WSR. When the content of LiAA exceeds 30 phr, the mass loss rate of WSR exhibits a quick increase as shown in Figure 5. This is because LiAA can generate PLiAA. The compatibility of LiAA and SBR matrix will become worse when the content of LiAA exceeds the critical value, leading to the separation of PLiAA and the immigration of PLiAA into water in the process of the absorption.

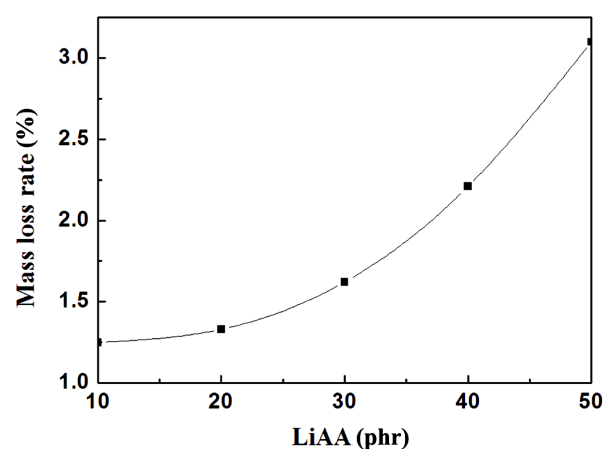The effect of the DCP content on the mass loss rate of WSR

Figure 4. Influence of TAIC content on the water absorption of WSR (Soak temperature: 25 ºC). Formula: SBR 100, SA 2, LiAA 30, DCP 3, TAIC variable.

Figure 5. Influence of LiAA content on the mass loss rate of WSR after swelled (Soak temperature: 25 ºC). Formula: SBR 100, SA 2, DCP 3, TAIC 2, LiAA variable.
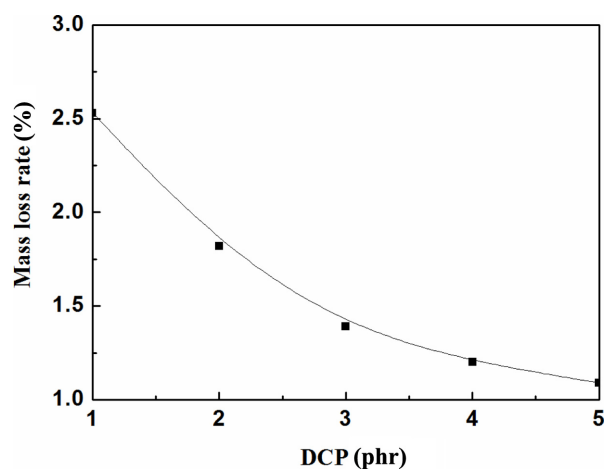
Figure 6. Influence of DCP content on the mass loss rate of WSR after swelled (Soak temperature: 25 °C). Formula: SBR 100, SA 2, LiAA 30, TAIC 2, DCP variable.
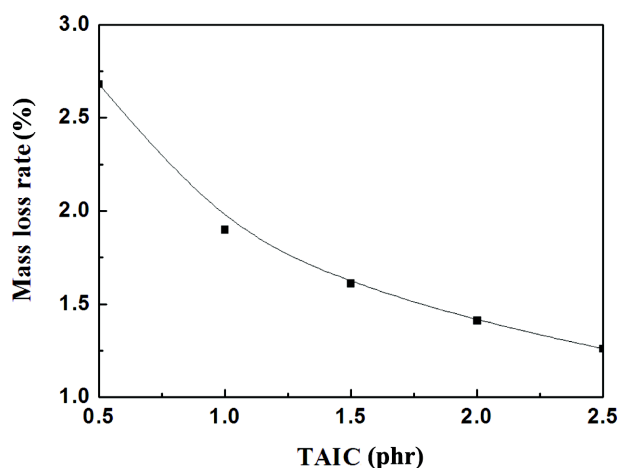

Figure 7. Influence of TAIC content on the mass loss rate of WSR after swelled (Soak temperature: 25 °C). Formula: SBR 100, SA 2, LiAA 30, DCP 3, TAIC variable.

Figure 8. SEM photographs of WSR with LiAA of 10 phr (a); 20 phr (b); 30 phr (c); 40 phr (d).

is shown in Figure 6. It can be seen that the mass loss rate of WSR gradually decreases with DCP content. When the content of DCP is higher than 3 phr, the mass loss of WSR is slightly declined. This is because DCP can severe as both the initiator and the crosslinking agent in the curing process. On one hand, DCP will initiate a polymerization of LiAA. On the other hand, it can promote the crosslink of SBR. When the content of DCP is low, the mesh structure is so unstable that PLiAA can easily get out of the SBR matrix. While the content of DCP exceeds 3 phr, the mesh structure is considerably close to retard the water absorption behavior of PLiAA due to the large crosslinking density.

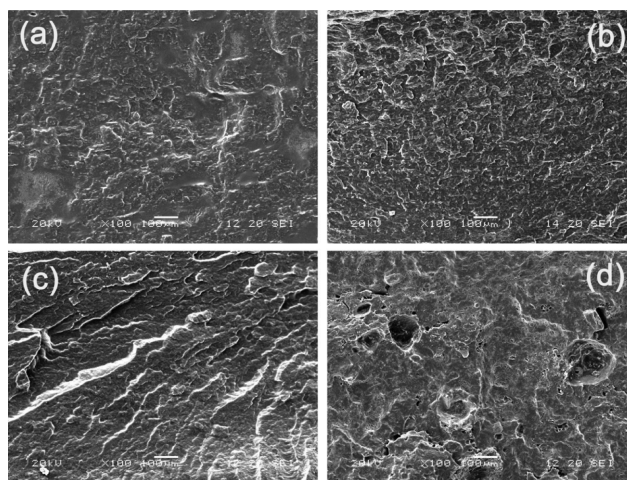The effect of TAIC content on the mass loss rate of WSR is shown in Figure 7. It can be seen that the mass loss rate of WSR gradually decreases with TAIC content. This tendency begins to become slow little by little when the content of TAIC is beyond 1 phr. The reason is that TAIC is the auxiliary cross-linking agent which can effectively enhance the crosslink degree of WSR during the curing process. In addition, TAIC can promote the polymerization of LiAA monomer. Further-more, the radicals come from the heated TAIC can also graft the PLiAA to SBR chain, leading to the improvement of the compatibility between SBR and PLiAA. When the content of TAIC exceeds 2 phr, the chance of the homogeneous cyclo-polymerization of TAIC[16] is greatly increased, which will lead to the decrease of the reaction efficiency of crosslinking.

SEM Photographs of the Fracture Surface for WSR. Figure 8 shows the SEM photographs of the fracture surface for WSR. The SEM photographs with 10~40 phr of LiAA are shown in Figure 8(a)~(d), respectively. The obvious differ-ences appear when the LiAA content is 30 phr. After the content increased to 40 phr, some voids can be seen on the fracture surfaces, indicating the separation of PLiAA from SBR matrix. Thus, the optimum LiAA content is 30 phr.

Conclusions

LiAA develops into PLiAA which has a reinforcing effect on WSR in the vulcanization process of styrene-butadiene rub-ber though *in-situ* polymerization. The optimum LiAA content to obtain the comprehensive performance is 30 phr. DCP can effectively improve the crosslinking density of WSR, and meanwhile decrease the mass loss rate of WSR. When the con-

tent of DCP is 3 phr, the WSR exhibits the maximum comprehensive performance. TAIC can promote the efficiency of DCP and improve the mechanical properties of WSR, and the optimum content of TAIC is 1 phr.

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