

Structural evolution of recycled tire rubber in asphalt

Hongru Yao, Shuai Zhou, Shifeng Wang

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai, China

Correspondence to: S. Wang (E-mail: shfwang@sjtu.edu.cn)

ABSTRACT: The performance of recycled-tire-rubber-modified asphalt mainly depends on the structure of rubber in the asphalt. The effects of the curing temperature, mixing time, and shearing on the evolution of the chemical structure and morphological structure of crumb rubber in asphalt were investigated. The crosslink density, compositions, and morphological evolution of the residual crumb rubber were characterized. The results show that the structure evolution of tire rubber in asphalt was greatly affected by the curing temperature. At a low curing temperature (180°C), the crosslinking network of the tire rubber was broken down, and this led to the partial dissolution of natural rubber (NR). However, at high curing temperature (240°C), the dissolution of NR, synthetic rubber, carbon black, and inorganic filler was observed. The released carbon black covered with a thin layer of bound rubber dispersed at a microstructured or nanostructured size in the asphalt. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42954.

KEYWORDS: crosslinking; morphology; recycling; rubber

Received 24 July 2015; accepted 18 September 2015

DOI: 10.1002/app.42954

INTRODUCTION

With the rapid development of the automotive industry, the number of discarded waste tires is increasing year by year. Recycling waste tires is a great challenge because of their three-dimensional crosslinking structure. The burning as fuel, pyrolysis, pulverization, and reclamation of waste tire rubber are the four typical recycling methods. Among them, pulverization into crumb rubber for the modification of asphalt has led to great interest because it disposes of waste and improves pavement performance.^{1–5}

The addition of crumb rubber directly into the asphalt mix results in a dry process that has not been widely used.⁶ This is mainly due to the undestroyed crosslinking structure of the crumb rubber and the weak interfacial adhesion between the crumb rubber and hot mixed asphalt. During a wet process or terminal blend process, the three-dimensional network breaks down at the crosslinking sites or in the main-chain bonds by a thermomechanical process. The interaction between asphalt and rubber is enhanced.^{7–9} Terminal blends have attracted a great interest because of the partial dissolution of rubber in asphalt; this not only reduces the cost of modified asphalt in the pavement but also makes the modified asphalt suitable for different kinds of hot mixed asphalt with different aggregates gradation, such as a dense-grade mixture, stone mastic asphalt, and an open-grade mixture. The size or status of the crumb rubber also has a great effect on the properties of asphalt pavement. A recent investigation also showed that the most effective way to

prevent trunk-crack formation in asphalt concrete is the addition of ultrafine rubber particles (150–750 nm) into a bituminous binder of asphalt.¹⁰

However, because of the extremely complex chemical natures and compositions of asphalt and crumb rubber, it is difficult to detect the real nature of chemical bonds and material exchange during the interaction between rubber and asphalt.^{11,12} Asphalt is known as a colloidal suspension in which asphaltenes are dispersed in the oily maltene phase. Crumb rubber is a complex mixture primarily comprised of natural rubber (NR) and synthetic rubber (SR), which are crosslinked with sulfur and reinforced with carbon black. Meanwhile, processing oils have been added to improve its workability and softness.¹²

Although the structural change of tire rubber in asphalt has been studied, the structure of the tire rubber in the asphalt is still unclear. Zanzotto and coworkers^{13–15} investigated the dissolution of crumb rubber in asphalt and the effects of different parameters on its rate and extent. The materials released from crumb rubber into the asphalt were found according to their molecular weight. The temperature, time, and mixing rate of the interaction have significant effects on the structural change of the crumb rubber. Ghavibazoo *et al.* investigated the effects of the crumb rubber source on its dissolution. They found that truck-tire rubber had more NR and dissolved faster than passenger-tire rubber.¹¹

The type and state of the released components from crumb rubber under each of the aforementioned conditions and their

Table I. Basic Properties of Zhonghai 70# Asphalt

Penetration at 25°C (0.1 mm)	Ductility at 25°C (cm)	Softening point (°C)	Viscosity at 135°C (Pa s)	Asphaltene (%)	Saturate (%)	Aromatics (%)	Resin (%)
70.3	>100	47.5	0.487	7.1	16.5	35.4	41.0

effects on the final properties of asphalt have been investigated for many years.^{16–22} Gawel *et al.*²³ showed that the linear aliphatic chains from asphalt penetrated into the crumb rubber structure, and the fatty acids from crumb rubber particles were released into the asphalt matrix under intermediate interaction conditions, where little crumb rubber dissolution occurred. As far as we know, none of these studies were able to define how the crosslinking network of rubber changed and what type and amount of the crumb rubber components were released into the asphalt matrix during its interaction with asphalt. The morphology of the interacted rubber in the asphalt was also not clear. To clarify the structural evolution process of tire rubber in asphalt on a microscopic scale is not only useful for optimizing the properties of crumb-tire-rubber-modified asphalt but also helpful for understanding the real function of tire rubber in asphalt pavement.

In this study, we investigated the crosslink density, composition, and microscopic morphology by running crosslinking measurements, compositional analysis, and electron microscopy on the residue of crumb-tire-rubber-modified asphalt after it was extracted with toluene. The effect of the structural evolution of tire rubber on the softening points of the crumb-rubber-modified asphalt was also investigated.

EXPERIMENTAL

Materials

Asphalt (Zhonghai 70#) was produced by China Ocean Oil Corp., and its basic properties are shown in Table I. The crumb rubber (size = 40 mesh) was an ambient ground rubber derived from whole truck-tire rubber manufactured by a local tire-

rubber recycling company. Carbon black (N330) was provided by Cabot Co., Ltd.

Preparation of Rubber-Modified Asphalt

Low-Cure-Rubber-Modified Asphalt. The base asphalt was heated to 180°C, which is a temperature that is often selected for conventional rubber-modified asphalt, and 20 wt % crumb rubber was added to the asphalt. The blend was stirred at 300 rpm for 60 min. The prepared crumb-rubber-modified asphalt was put into an oven at 180°C. Samples were taken out from the modified asphalt every 3 h for further analysis.

High-Cure-Rubber-Modified Asphalt. The base asphalt was heated to 180°C, and 20 wt % crumb rubber was added to the asphalt. Then, the temperature was quickly improved to 240°C; this is often selected as the terminal blend temperature. Samples were taken out at 3, 5, 15, 30, and 60 min, respectively.

Characterization

Extraction of Crumb-Rubber-Modified Asphalt. To clarify the changes in the crumb rubber after interaction, Soxhlet extraction was used to separate the soluble fraction from the blend. The crumb-rubber-modified asphalt (ca. 2.5 g) was wrapped with filter paper and extracted by toluene for 24 h. The processing oil, sol fraction of the crumb rubber, and asphalt were soluble in toluene. The insoluble part was dried further in a vacuum oven at 110°C for 1.5 h after the solvent was first vaporized in the ventilated hood, and thus, a residue was left.

Softening Points of the Crumb-Rubber-Modified Asphalt. The softening points were tested according to ASTM D 36-06.

Thermogravimetric Analysis (TGA). TGA (TGA-Q5000 from TA Corp.) analysis was carried out under N₂ gas with a flow rate of 50 mL/min. The measuring temperature rate was

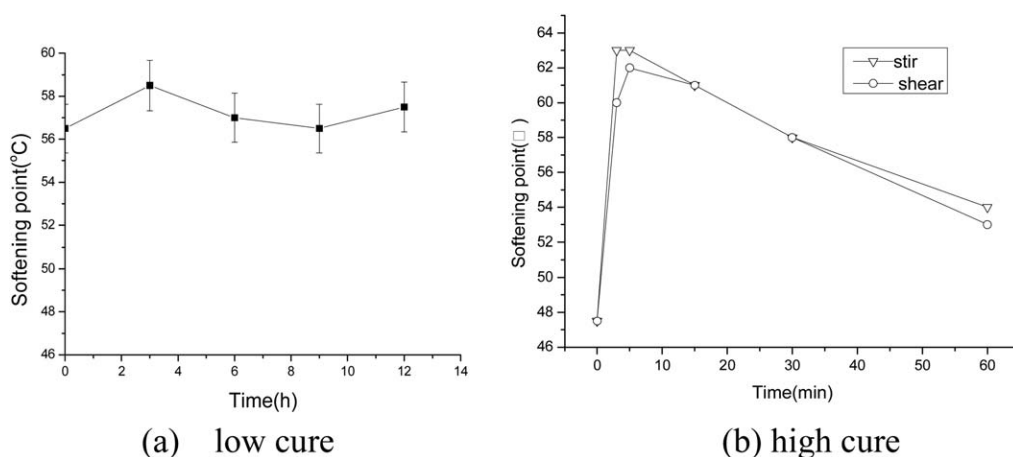


Figure 1. Softening points of crumb-rubber-modified asphalt during different curing processes.

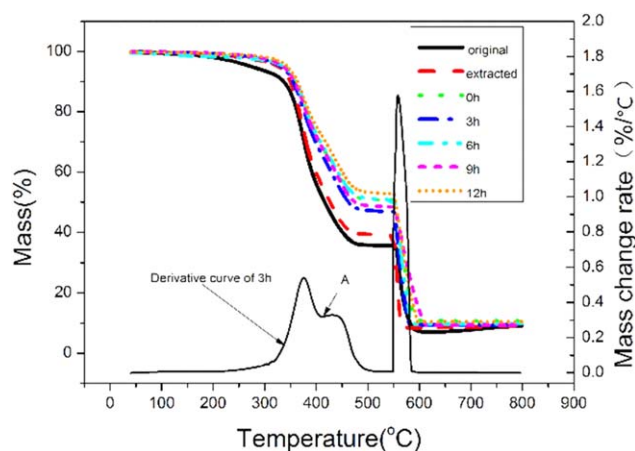


Figure 2. TGA curves of the original and residual crumb rubber after a low cure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

10°C/min, and the temperature range was from room temperature to 550°C. To calculate the content of carbon black and inorganic filler, the gas atmosphere was changed to air and heated further to over 700°C. For statistical analysis, TGA was repeated on the residue samples. Less than a 3% variation was observed as a result, and this proved the high repeatability of this test method.

Crosslink Density. The residue was milled into a thin sheet (1 cm² with a thickness of 0.2 mm) by a two-roll mill for the measurement of the crosslink density. The sheets were put into toluene for the swelling test until swelling equilibrium was reached at 25°C.

The swelling degree (Q) was calculated according to eq. (1):

$$Q = \left(\frac{w_1}{\rho_1} + \frac{w_2}{\rho_2} \right) / \frac{w_2}{\rho_2} \quad (1)$$

where w_1 and w_2 are the masses of the toluene absorbed by rubber and the rubber, respectively, and ρ_1 and ρ_2 are the densities of toluene and rubber, respectively.

The crosslink density was calculated according to eq. (2):

$$\bar{M}_c = \rho_2 \tilde{V}_1 Q^{5/3} / (0.5 - \chi_1) \quad (2)$$

where \bar{M}_c is the average molecular weight between two crosslinking points, \tilde{V}_1 is the molar volume of the solvent, χ_1 is the interaction parameter between rubber and toluene, and 0.40 was adopted according to ref. 24.

Microscopic Morphology. The residual samples were diluted and dispersed with toluene. A small amount of suspension was put onto the aluminum sheet. The samples were platinum-coated after the evaporation of toluene. Then, the microscopic morphology was determined with high-resolution scanning electron microscopy (SEM; JEOL JSM-7401F). SEM coupled to an energy-dispersive X-ray spectrometer was used to obtain the compositions of the released materials. The released carbon black was diluted and dispersed with toluene. A small amount of suspension was dropped onto the copper grids (300 mesh). The morphology of carbon black was determined with a trans-

Table II. Calculated Compositions of the Original Crumb Rubber and Residue under a Low Cure

Sample	Soluble (%)	Residue (%)			
		NR	SR	Carbon black	Inorganic
Original rubber	5.9	46.8	14.0	27.0	6.4
0 h	28.0	22.6	12.8	28.7	7.9
3 h	32.2	22.6	13.3	25.4	6.5
6 h	34.6	20.1	11.8	26.9	6.6
9 h	38.2	19.7	12.1	24.1	5.9
12 h	40.0	16.6	11.7	25.4	6.3

mission electron microscope (JEOL JEM-2100) with voltage of 200 kV.

RESULTS AND DISCUSSION

Effect of the Curing Temperature on the Softening Points

The softening point is a typical and conventional property representing the heat resistance of asphalt. It can be used as an index indicating the interaction between crumb rubber and asphalt. As shown in Figure 1, the softening points of the crumb-rubber-modified asphalt increased at first and then decreased. When the crumb rubber interacted with asphalt, the saturates (saturated hydrocarbons) and naphthene aromatics (consisting of partially hydrogenated polycyclic aromatic compounds) of asphalt were absorbed by crumb rubber; this led to an increase in the solid volume in the asphalt. The resin (consisting of high-molecular-weight phenols and carboxylic acids) and asphaltene (consisting of high-molecular-weight phenols and heterocyclic compounds) also condensed and formed strong interactions; this significantly improved the high-temperature properties of the modified asphalt.^{25,26} The crumb rubber partially degraded and released polymer and absorbed oil into the asphalt with extended storage times. The dissolution of rubber

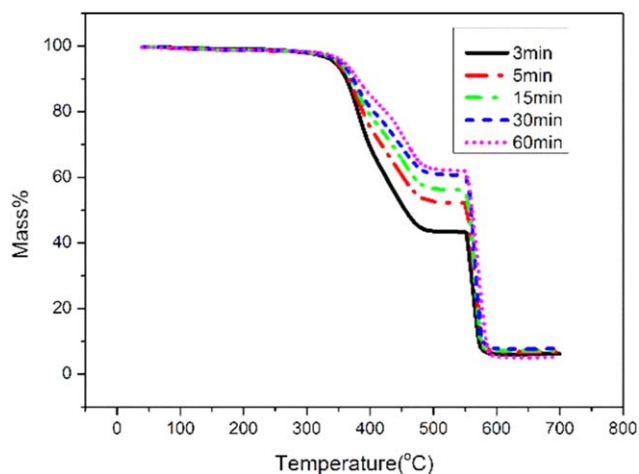


Figure 3. TGA curves of residual rubber after a high cure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

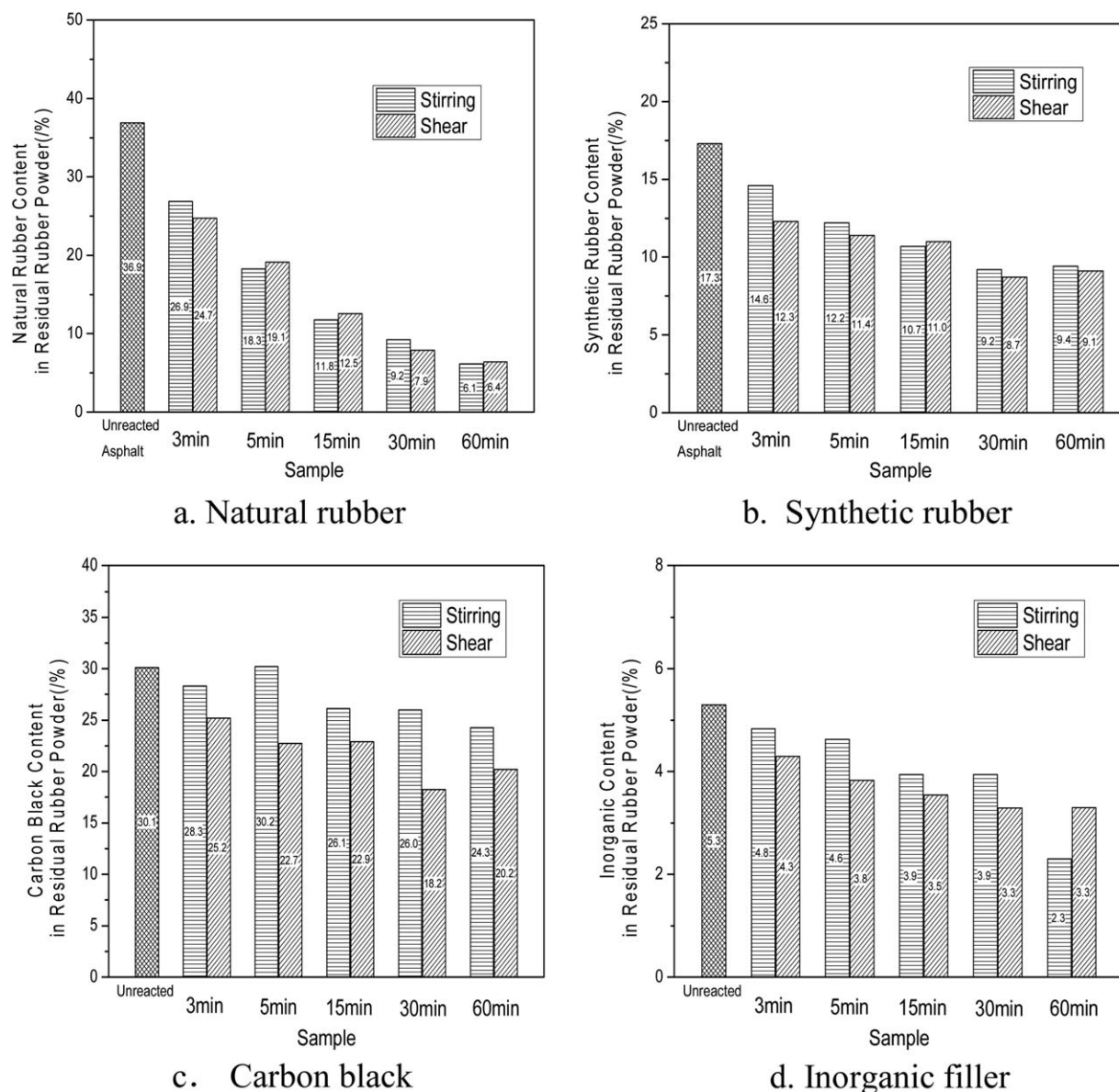


Figure 4. Evolution of different compositions in tire rubber under high curing conditions.

resulted in a decrease in the softening points of the crumb-rubber-modified asphalt.

As shown in Figure 1(a), the softening points of the crumb-rubber-modified asphalt increased in the initial storage time and decreased slowly after 3 h. In a comparison of the crumb rubber interacting with the asphalt at the low curing temperature, the softening points decreased faster at the high curing temperature, as shown in Figure 1(b); this indicated that the crumb rubber degraded quickly under these conditions. The

details of the dissolving process and the compositional change were further analyzed with TGA and microscopic observation.

TGA

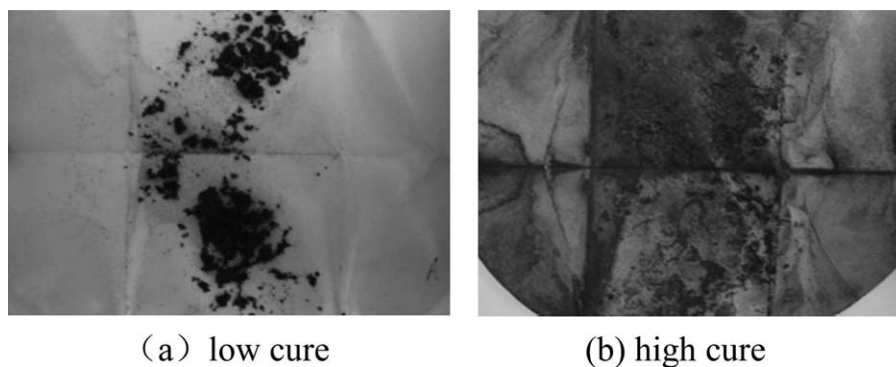
TGA is a useful tool for clarifying the composition of tire rubber.^{27–29} As shown in Figure 2, point A is a peak minimum in the derivative curve of TGA; this is also considered as the dividing point of NR and SR.¹¹ The weight loss between 300°C to temperature A was due to the decomposition of NR, whereas the weight loss from temperature A to 550°C was due to the

Table III. Changes in the M_c Values of the Residue under a Low Cure

Stir time	Original	0 h	3 h	6 h	9 h	12 h
M_c (g/mol)	2520	2973	3317	4937	5665	5430

Table IV. Changes in M_c of the Residue under a High Cure

Sample	Original	3 min	5 min	15 min	30 min	60 min
Stir (g/mol)	2520	7305	5608	4388	3367	2264
Shear (g/mol)	2520	5336	7130	4635	3768	3676



(a) low cure (b) high cure

Figure 5. Morphology of residual rubber after low and high curing.

decomposition of SR. The weight loss between 550 and 700°C was due to the decomposition of carbon black, and the residue was inorganic filler. The details of the composition of the crumb rubber during the interaction are listed in Table II. As shown, the content of NR decreased significantly with increasing interaction time, whereas the content of SR decreased a little. The content of carbon black increased relatively because of the partial dissolution of NR. The content of inorganic filler showed almost no change during the whole process.

As shown in Table II, the quantity of dissolved rubber estimated from the extraction method increased from 5.9% (original rubber) to 40.0% (after 12 h of interaction) when the crumb rubber interacted with asphalt at the low curing temperature. The content of NR decreased obviously from 46.8 to 16.6%, as esti-

mated from TGA, whereas the SR, carbon black, and inorganic residue showed a slight change compared to NR. The result was in agreement with research by Ghavibazoo.¹¹ This was mainly because SR consisting of SBR had aromatic groups, and this inferred thermal resistance to covalent bonds. The NR of the crumb rubber decreased from 46.8 to 22.6% during processing, and the decrease became much less pronounced; it was only of 6% after 12 h of storage. This indicated that the NR dissolved into the asphalt very fast during the initial processing stage and slows down during the later storage stage.

The TGA results of the residue after curing at the high temperature are shown in Figure 3. The contents of NR and SR decreased a lot compared to those at the low curing temperature. The decreasing rate slowed down when the curing time

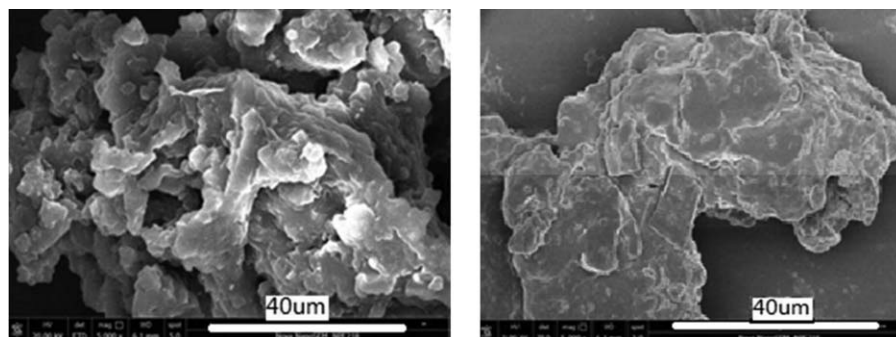


Figure 6. Morphology of original crumb rubber and residual rubber after a low cure.

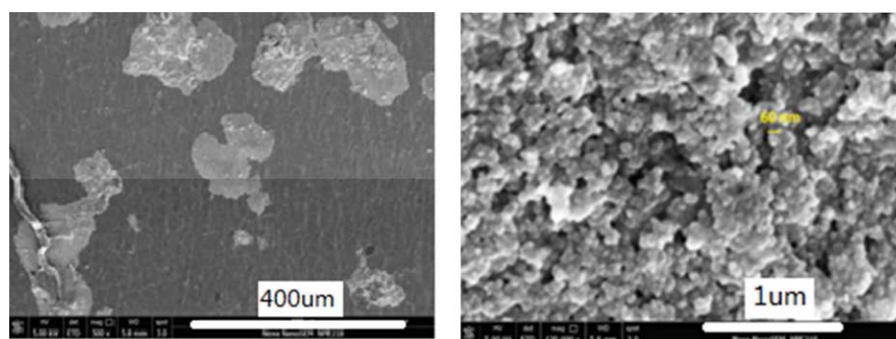


Figure 7. Surface of some residual rubber after a 60-min high cure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

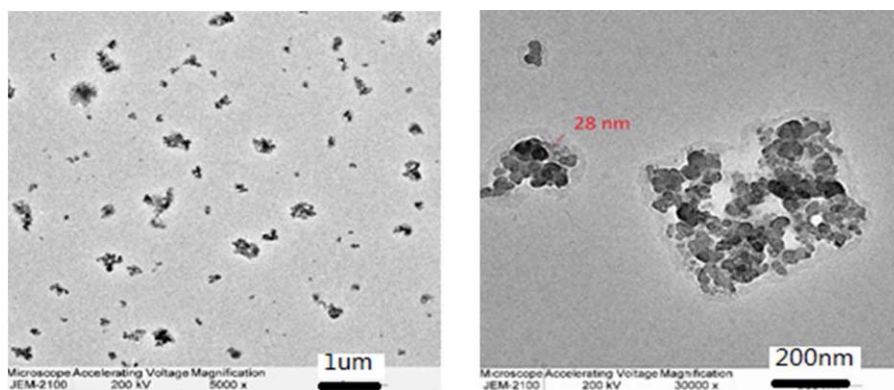


Figure 8. Released carbon black in the asphalt. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was extended past 15 min. The content of carbon black increased obviously in the residue, whereas the content of inorganic filler showed a slight decrease. To understand the evolution of different compositions of tire rubber during high curing conditions, their relative content as a function of time were calculated and are listed in Figure 4.

As shown in Figure 4(a,b), both NR and SR were released into asphalt under high curing conditions. The degree of release of NR was slower than that of SR. It seemed that high shear made more NR or SR be released into asphalt. The content of carbon black and inorganic filler decreased with increasing curing time, as shown in Figure 4(c,d). This indicated that these inorganic materials could be released into asphalt under high curing conditions; this was different from the behavior under low curing conditions. A high shear obviously promotes the dispersing ability of inorganic materials into asphalt comparing with stirring.

Crosslink Density Change of the Residual Rubber

The crosslink density is one of the most important parameters for vulcanized rubber.²⁶ As shown in Table III, M_c increased with curing time. This was mainly due to the main-chain or crosslinking chain scission during the low curing process; this also led to the partial dissolution of NR. M_c increased obviously after 3 h of interaction, and this was consistent with the fast decrease of softening points shown in Figure 1.

As shown in Table III and Table IV, M_c gradually decreased, and this indicated that the crosslink density increased. The main reason was the dissolution of NR into the asphalt; this reduced the percentage of low crosslink density. In the later stage, the crosslinking structure of SR was harder to break. Some new crosslinking points were even formed, and this increased the crosslink density. On the other hand, the increase in the carbon black and inorganic filler led to a decrease in the absorption of toluene into the residual crumb rubber, and this reduced Q .

Morphological Observations

The statuses of the residual rubber after low curing and high curing are presented in Figure 5. This clearly shows that the crumb rubber retained its original shape without a great change after curing at the low temperature. The crumb rubber was finely dispersed after curing at the high temperature. Some car-

bon black penetrated across the filter paper, and some dispersed onto the filter paper.

SEM micrographs of the original crumb rubber and residue extracted from the low-cure rubber asphalt are presented in Figure 6. It was clear that the original crumb rubber had lots of porosity because of the grinding process of crumb rubber production under ambient conditions. Smooth angular surfaces were observed after the low-curing interaction. This observation implied that the particles lost roughness during their interaction with asphalt; this may have been caused by the dissolution of rubber at the surface.

SEM micrographs of the samples after high curing are shown in Figure 7. The images show clearly that there was lots of carbon blacks dispersed evenly in the rubber matrix at the size of 60 nm; some of the carbon black was released into the asphalt and left voids on the surface of the rubber.

Transmission electron micrographs of the released carbon black are shown in Figure 8. The residue of the high-cure rubber consisted of carbon black around microsize. From the high-magnification image, it can be observed that the carbon black was covered by a thin layer of bound rubber with a thickness of 28 nm. The released carbon black had three forms, initial particles with a size of 30 nm, aggregates with a size of 200 nm, and the third agglomerate, which consisted of several aggregates. The compositions of this released carbon black was analyzed by SEM–energy-dispersive X-ray spectrometer (EDX) (Table V). In a comparison to the original carbon black N330, the released carbon black had a lower O content; this indicated that the surface of released carbon black was encapsulated by a thin layer of bound rubber. Zn appeared in the released carbon black after high curing, as is also illustrated by TGA. According to rubber–filler interface model of a carbon-black-filled rubber, the

Table V. Compositions of the Released Carbon Black Analyzed by SEM–EDX

Element	C	O	S	Zn
Carbon black N330 (%)	84.09	11.12	3.13	0
Released carbon black (%)	79.91	1.74	3.45	8.97

double-layer consisted of an inner polymer layer in a glassy state.²⁴ The molecular motion in both layers was considerably constrained because of strong molecular packing. Therefore, strong filler–rubber bonds were not affected during the high-cure process and remained as bound rubber.

CONCLUSIONS

The structural evolution processes of tire rubber in asphalt at low and high curing temperatures were investigated in terms of chemical and morphological aspects. The following conclusions were obtained from the previous discussion. After tire-rubber curing at low temperature in asphalt, the softening points of the rubber asphalts gradually decreased because the breakdown of the crosslinking network led to a partial dissolution of rubber. NR was more prone to dissolving into the asphalt compared to SR. The softening points sharply decreased at the high curing temperature because the quick degradation of the crosslinking network led to the severe dissolution of rubber. The dissolution percentage was around 60%, and the remaining contents of NR and SR were 6 and 9%, respectively. The high shear force promoted the release of the carbon black and inorganic fillers into the asphalt at the high curing temperature; this caused a lot of carbon black with a size of 60 nm to appear on the surface of the residual rubber. The released carbon black was covered with a thin layer of rubber with a thickness of about 28 nm.

ACKNOWLEDGMENTS

This work was supported by the International Cooperation Project of Ministry of Science & Technology of China (contract grant number 2013DFR50550) and the National Natural Science Foundation of China (contract grant number 51273110). Special thanks go to the researchers of the Institute of Analysis at Shanghai Jiao Tong University for their helpful tests and analysis.

REFERENCES

1. Navarro, F. J.; Partal, P.; Martínez-Boza, F.; Gallegos, C. *Fuel* **2004**, *83*, 2041.
2. Kök, B. V.; Çolak, H. *Constr. Build. Mater.* **2011**, *25*, 3204.
3. Wang, H.; Dang, Z.; Li, L.; You, Z. *Constr. Build. Mater.* **2013**, *47*, 1342.
4. Navarro, F. J.; Partal, P.; Martínez-Boza, F.; Gallegos, C. *Energy Fuels* **2005**, *19*, 1984.
5. Lo, P. D. *Constr. Build. Mater.* **2013**, *49*, 863.
6. López-Moro, F.; Javier, M. M. C.; Hernández-Olivares, F.; Witoszek-Schultz, B.; Alonso-Fernández, M. *Constr. Build. Mater.* **2013**, *48*, 691.
7. Thives, L. P.; Pais, J. C.; Pereira, P. A. A.; Trichês, G.; Amorim, S. R. *Constr. Build. Mater.* **2013**, *47*, 431.
8. Fontes, L. P. T. L.; Trichês, G.; Pais, J. C.; Pereira, P. A. A. *Constr. Build. Mater.* **2010**, *24*, 1193.
9. Billiter, T. C.; Chun, J. S.; Davison, R. R.; Glover, C. J.; Bullin, J. A. *Pet. Sci. Technol.* **1997**, *15*, 445.
10. Kaplan, A. M. In *Times of Polymers (TOP) and Composites*; AIP Conference Proceedings Volume 1599; American Institute of Physics: Melville, NY, **2014**; p 542.
11. Ghavibazoo, A.; Abdelrahman, M. *Int. J. Pav. Eng.* **2013**, *14*, 517.
12. Miknis, F. P.; Michon, L. C. *Fuel* **1998**, *77*, 393.
13. Zanzotto, L.; Kennepohl, G. J. *Trans. Res. Rec.* **1996**, *1530*, 51.
14. Billiter, T. C.; Davison, R. R.; Glover, C. J.; Bullin, J. A. *Pet. Sci. Technol.* **1997**, *15*, 205.
15. Celik, O. *Constr. Build. Mater.* **2008**, *22*, 1143.
16. Abdelrahman, M. A.; Carpenter, S. H. *Trans. Res. Rec.* **1999**, *1661*, 106.
17. Frantzis, P. *J Mater. Civ. Eng.* **2004**, *16*, 387.
18. Abdelrahman, M. *Transport. Res. Rec.* **2006**, *1962*, 64.
19. Leite, L. F. M.; Soares, B. G. *Pet. Sci. Technol.* **1999**, *17*, 1071.
20. Huang, S. C. *J Mater. Civ. Eng.* **2008**, *20*, 221.
21. Huang, S. C.; Pauli, A. T. *Road Mater. Pav. Design* **2008**, *9*, 73.
22. Airey, G. D.; Rahman, M. M.; Collop, A. C. *Int. J. Pav. Eng.* **2003**, *4*, 105.
23. Gawel, I.; Stepkowski, R.; Czechowski, F. *Ind. Eng. Chem. Res.* **2006**, *45*, 3044.
24. Saiwari, S.; Dierkes, W. K.; Noordermeer, J. W. M. *Kautsch. Gummi Kunstst.* **2013**, *7*, 20.
25. Lu, X.; Isacson, U. *Polym. Test* **2000**, *20*, 77.
26. Airey, G. D. *Fuel* **2003**, *82*, 1709.
27. Fernández-Berridi, M. J.; González, N.; Mugica, A.; Bernicot, C. *Thermochim. Acta* **2006**, *444*, 65.
28. Lee, Y. S. *J. Anal. Appl. Pyrolysis* **2007**, *78*, 85.
29. Chen, F. Z.; Qian, J. L. *Waste Manage.* **2003**, *23*, 463.