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Antioxidation efficiency and reinforcement performance of precipitated-silica-based immobile antioxidant obtained by sol method in natural rubber composites

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Abstract

Tetraethoxysilane-40 (TEOS) was hydrolyzed in alkaline environment to prepare sol precursor consisting of large amount of silicic acid oligomers, and then the silicic acid oligomer was grafted with 4-aminodiphenylamine (RT) which was the intermediate of antioxidant-4010NA (AO) via silane coupling agent 3-glycidoxypropyltrimethoxysilane (KH-560), generating the precipitated-silica-based antioxidant (P-RT) through the condensation polymerization. Fourier transform infrared spectroscopy (FTIR) test demonstrated that RT has been successfully grafted onto the surface of precipitated silica. Thermogravimetric analysis (TGA) results exhibited the high grafting efficiency of this sol-grafting method. The massive grafted antioxidant groups took the same role as the traditional surface modifier bis (3-triethoxysilylpropyl) tetrasulfide (TESPT). According to the results of tensile tests, the reinforcement performance of P-RT was better than that of the silica modified by TESPT in natural rubber matrix. The oxidation induction time (OIT) tests and accelerated aging tests revealed that P-RT possessed much better anti-oxidative and anti-migratory efficiency than that of the corresponding low molecular counterpart (4010NA).

Introduction

Natural rubber (NR) is well-known for its various excellent properties, such as rebound resilience, insulativity and abrasion resistance, but it still needs to be reinforced by filler in practical application [1, 2]. In the tire industry, both silica and carbon black (CB) are used as reinforcing fillers for rubber matrix, and silica can improve the abrasion resistance, tear strength and aging resistance of NR matrix more significantly. Particularly, NR/silica tire product possesses far lower rolling resistance in contrast with NR/CB tire product so that silica has attracted more and more attention in reinforcing NR [3-6].

On the surface of silica, there are massive silanol groups, leading to the strong polarity of silica. Therefore, the highly polar silica has a poor compatibility with the non-polar NR matrix, which results in the weak interaction between the silica and NR. It's necessary to reduce the concentration of silanol groups on the surface of silica through surface modification before use, otherwise the incorporation of silica will make no contribution to the improvement of rubber performance [7, 8]. At present, the common surface modification treatment for silica is the addition of coupling agent during mixing, such as bis (3-triethoxysilylpropyl) disulfide (TESPD) and bis (3-triethoxysilylpropyl) tetrasulfide (TESPT). The coupling agent can react with the silanol groups and chemically connect the silica with the rubber matrix [9, 10]. Moreover, Roberto Scotti et al. applied in situ sol-gel method to prepare rubber-silica nanocomposites, in which silica was grafted onto the natural rubber molecule, and the results showed that the dispersion state of silica in NR matrix was much better than that of physical blending system [11]. But the grafting efficiency of silica in NR

matrix was low, and the production cost of the in situ sol-gel method was high.

Because of the existence of large amount of unsaturated bonds on NR molecule, NR is easy to undergo degradation, when it is exposed to thermal, oxidative or radiant condition, resulting in the shortened service life of NR [12, 13]. To postpone the aging of NR, the antioxidant is incorporated into NR matrix, such as 4010NA, 4020 and aminophenol, which can prevent the formation of free radical and wipe out the generated radical or hydroperoxide during the aging of NR [14]. However, these low molecular weight antioxidants are apt to volatilize and escape from the NR composites, which gives rise to the reduction of anti-aging efficiency and pollution to environment. Furthermore, if too many antioxidants are added into the rubber matrix for enhancing the anti-oxidation performance, the blooming of antioxidants will appear on the surface of rubber, degrading the performance of rubber products [15, 16].

In order to eliminate the drawbacks of antioxidant, different solutions have been proposed, such as enlarging the molecular weight of antioxidant, grafting the antioxidant onto the rubber molecular chain and grafting the antioxidant onto the filler [17, 18]. Abd El-Aziz El-Wakil et al. grafted the o-aminophenol onto the NR molecular chain, and found that the NR-based antioxidant can improve the thermal oxidation resistance of nitrile rubber a lot, but the high cost of this method limited its application [19]. Moreover, enlarging the molecular weight of antioxidant via its polymerization can't solve the problem fundamentally, because the volatilization of the antioxidant is still inevitable in harsh conditions, and the dispersity of

macromolecular antioxidant is poor in rubber matrix [20-23].

By comparison, grafting the antioxidant onto the filler is a more effective method, which can not only fix the antioxidant molecule on the filler but also play an important role as the surface modifier for filler. In our previous paper, we have prepared the silica-based antioxidant (RT-silica) where RT was grafted onto the fumed silica successfully, and the results showed that RT-silica could improve the anti-aging performance and mechanical property of styrene butadiene rubber (SBR) composites [24]. However, the three-dimensional network structure of silica leaded to its insolubility, so it was difficult to perform the grafting reaction on the surface of silica, bringing about that the content of grafted antioxidant on the surface of fumed silica was too low to make a difference of surface modification to the fumed silica. Therefore, if the filler concentration was lower than 10%, RT-silica and fumed silica had the similar reinforcement effect on SBR matrix, and only when the high content of fillers were incorporated into SBR matrix (30 phr), RT-silica showed more excellent reinforcement performance than the general fumed silica [25].

In this paper, we creatively grafted the antioxidant onto the silicic acid oligomer, and then took advantage of the silanol condensation reaction of silicic acid oligomers to obtain the precipitated-silica-based immobile antioxidant (P-RT) of high grafting efficiency, which has been confirmed by TGA and FTIR tests. Due to the chemical grafting, P-RT avoided the blooming of antioxidant at high content and showed well dispersion state in NR matrix. According to the tensile tests, even low content of P-RT (10 phr) exhibited more significant reinforcement performance on NR matrix than

that of silica modified by TESPT, revealing the higher surface modification efficiency of P-RT. The anti-oxidation efficiency of P-RT was far higher than that of the corresponding low molecular weight antioxidant 4010NA (AO), which was investigated by OIT test and accelerated aging measurement. After we applied TESPT to link P-RT with the cross-linking network of NR, a complete network was formed in vulcanized NR composites where the silica, antioxidant and rubber molecular chain were chemically bonded to each other, making NR/P-RT/TESPT possess amazing performance.

Experimental

Materials

Tetraethoxysilane (content of $SiO_2 > 28\%$) was provided by Tianjin Bodi Chemical Industry (China). The silane coupling agent 3-glycidoxypropyltrimethoxysilane (KH-560, purity 98%) and the reactive antioxidant intermediate 4-aminodiphenylamine (RT, purity 98%) were purchased from Aladdin Inc. (China) which were used as received. Toluene, absolute ethyl alcohol and acetone used in this study were reagent grade. NR SCRWF was supplied by Xishuangbanna Dongfeng farm (China). Stearic acid, N-Isopropyl-N'-phenyl-4-phenylenediamin (4010NA), N-cyclohexyl-2-benzothiazole sulfenamide (CZ), and sulfur were of commercial grade. Ammonia water (purity 28%) was provided by Jinshan Inc. (China).

Preparation of sol precursor and precipitated silica

TEOS, absolute ethyl alcohol and deionized water were mixed at the ratio of 5: 4: 2. Ammonia water was used to adjust the pH of the mixed solution to ~8. Then the

mixture was stirred at 60 ℃ for 2 h to form the sol precursor. If the hydrolysis reaction time was more than 5 h, a lot of white precipitation will be generated. Then the white precipitation was dried in vacuum oven at 120 ℃ to obtain the precipitated silica. Fig.1 shows the hydrolysis reaction of forming silicic acid oligomer.

Preparation of P-RT

RT (4.5 g) was dissolved in the toluene (150 ml). Then KH-560 was instilled in the solution gradually and the mixed solution was stirred at 85 ℃ for 4 h. After 4 h, sol precursor (100 ml) was added into the mixed solution and stirred for 48 h with the temperature of 100 ℃. Then the solution was filtered to obtain solid mixture. The solid mixture was dried in a vacuum oven at 70 ℃ for 12 h. Finally, the solid mixture was extracted via acetone to remove the unreacted RT for 72 h. The product named as P-RT was dried in a vacuum oven at 70 ℃ for 24 h before use. The synthesis procedure of P-RT is presented in Fig.2.

Preparations of NR/silica composites

The NR composites were prepared via a two-roll mill for 10 min at room temperature. First, the raw NR was plasticated on a two-roll mill and then SA, CZ, ZnO, silica, TESPT and sulfur were added onto the mill to mix with NR matrix evenly. The mixed rubber elastomer was placed for 24 h at least before vulcanization. Then these elastomer mixture were vulcanized at 143 ℃ under the pressure of 15 MPa for t_{90}. Finally, the vulcanized rubber was tailored in an average thickness of 2 mm. The contents of ingredients of these NR/silica composites are listed in Table.1. According to TGA results, the contents of precipitated silica and 4010NA were fixed at 7.46%

and 1.23%, respectively, which took the content of absorbing water in the precipitated silica into consideration. The loading of TESPT was fixed at 2.82%, which was equal to the total content of grafted antioxidant and KH560 in NR/P-RT composite.

Determination of bound rubber content

First, the mixed NR elastomer without vulcanizing agent was prepared on the two-roll mill. The components of the NR elastomer are listed in Table.2. The elastomer mixture was placed for 72 h at least, which made the filler interact with NR matrix adequately. Then the elastomer mixture was extracted in toluene solution. After 7 days, the undissolved rubber was filtered and then dried in the vacuum oven at 50 ℃ for 24 h. The weight of the residual rubber was measured. Then the content of bound rubber (ω_B) in NR composites can be determined from the equation [26]:

$$\omega_B(\%) = \frac{m_2}{m_1} * 100$$

where the m_1 is the rubber weight in the initial elastomer mixture and m_2 is the weight of residual rubber after extraction.

Extraction Experiments

The vulcanizates of NR, NR/silica/AO, NR/P-RT, NR/silica, and NR/AO were immersed in deionized water in glass beakers. The temperature was maintained at 50℃ by a thermostat water bath. The samples were extracted for different time and then taken out for OIT test. OIT is the time interval between initiation of oxygen flow and the onset oxidation in differential scanning calorimetry (DSC) measurement, which is

used to evaluate the anti-oxidation performance of material. The deionized water

was changed every 12 h. The migration of antioxidant can be investigated through

the change tendency of OIT.

Measurements

Fourier transform infrared spectra (FTIR) were conducted on a Perkin–Elmer–

System 2000 infrared spectrum analyzer with KBr pellets in the wave number range

from 4000 to 400 cm^{-1}. The scanning was performed 32 times with a resolution of 4

cm^{-1}. TG was carried out on Mettler Toledo TGA/DSC 1 instrument to determine the

content of grafted antioxidant on P-RT. The samples were heated from room

temperature up to 800℃ at a heating rate of 20℃/min in air. OIT test was

performed by DSC on a TA Q200 instrument according to the standard method (ISO

11357-6, 2002). This method is illustrated as followed, the sample was held at 40℃

for 5 min with a nitrogen flow of 50 ml/min to remove the air, and then the sample

was heated with a heating rate of 10℃/min to 140℃ and maintained for 7 min. At

this time, nitrogen was replaced by oxygen at a flow rate of 50 ml/min. Then, an

exothermic peak appeared resulting from the thermal oxidation of NR composites.

The OIT value can be obtained from recording the time interval from oxygen flow to

the onset point of exothermic peak. Scanning electron microscopy (SEM) images

were observed on an Inspect F at 20 kV. Instron 5567 material testing machine (with

a 1 kN load cell) was applied to measure the stress-strain curve at room temperature

with extensional strain rate of 500 mm min^{-1} in accordance with the GB/T1040-92.

The initial thickness and length of the samples were 2 and 15 mm. Each test chose an

average value of five parallel samples. All samples for accelerated aging test were aged in air condition at 85 ℃ for different time.

Results and discussion

Characteristic of the grafted antioxidants on the surface of precipitated silica

The reaction process of synthesizing P-RT was that the primary amino group of RT first reacted with the epoxy group of KH560, and then the methoxy group of KH560 reacted with the hydroxyl of silicic acid oligomer, which was interpreted through FTIR and TGA.

Fig.3 is the infrared spectrum of P-RT and precipitated silica. In Fig.3.a, the broad strong band between 3700 and 3200 cm^{-1} in the spectrum of P-RT and precipitated silica belongs to the stretching vibration of silanol groups and absorbed water. Compared with the spectrum of precipitated silica, several new characteristic peaks appear in the spectrum of P-RT. The peaks at 2877 and 2932 cm^{-1} are attributed to the stretching vibration of C-H in methylene group which is the characteristic group of KH560, indicating that the structure of KH560 is a moiety of P-RT. Fig.3.b is the partial enlarged detail of the spectrum between 1700 and 1400 cm^{-1}, in which three emerging absorption peaks appearing at 1497, 1518 and 1600 cm^{-1} are assigned to the characteristic peaks of benzene ring, demonstrating the existence of the structure of RT in P-RT [24]. Owing to the strict extraction to the samples before FTIR test, there is no unbonded RT and KH560 in P-RT sample. Hence, it can be concluded that RT has been successfully grafted onto the surface of precipitated silica via the coupling agent KH560.

The TGA results of precipitated silica and P-RT are showed in Fig.4 from which it can be found that the mass loss of general precipitated silica is 6.54 wt%, whereas the mass loss of P-RT increases to 31.41 wt% after the grafting reaction. In contrast with the precipitated silica, the extra mass loss of P-RT is attributable to the mass loss of grafted RT and KH560. The mass loss of precipitated silica before 100 ℃ is due to the volatilization of absorbed water, so the actual mass loss of silica is about 2 wt%. However, P-RT only lose the weight of 1.2% before 100 ℃, indicating that this surface modification method of grafting antioxidant can weaken the water-absorbing capacity of silica, as a result of the reduction of hydrophilic hydroxyl on the surface of silica. The change in the hydroscopicity of P-RT confirms that the hydroxyl groups indeed react with KH560. Because of the high reactive efficiency between the epoxy group of RT and the primary amine of KH560, there is little silica which only reacts with KH560. Therefore, the stoichiometry of the reaction between RT and KH560 can be seen as 1: 1 [24]. Considering the content of absorbing water in the precipitated silica and P-RT, the loading of grafted antioxidant on P-RT is 12.27 wt% and the loading of silica is 71.79 wt%.

Morphology and dispersion of P-RT in NR matrix

SEM test was applied to observe the dispersion state of silica and P-RT in NR matrix, and the results are showed in Fig.5. It can be found that the dispersity of precipitated silica in NR/silica/AO composite is very poor as shown in Fig.5.b, where the precipitated silica form a number of large aggregations whose average size are about 800-900 nm. The dispersion state of filler in NR/P-RT is much better compared

with that in NR/silica/AO composite. With the incorporation of TESPT, silica possesses the similar dispersity in NR/silica/TESPT composite with that of P-RT in NR matrix as shown in Fig.5.c and Fig.5.d, in which the fillers form the aggregations of 400-500 nm. The most surprising is that P-RT shows the best dispersity in NR/P-RT/TESPT composite where the size of the aggregation formed by P-RT is about 100-200 nm.

As the natural rubber is one kind of non-polar rubber, the unmodified silica with polar hydroxyl groups has low compatibility with NR matrix. Besides, the silicon hydroxyl groups make the silica particles have a strong tendency to react with each other via silanol condensation, forming aggregations of large size in quantity [27, 28]. The numerous and polar hydroxyl groups on the surface of silica lead to the poor dispersity of precipitated silica. However, both the grafted KH560-antioxidant and TESPT can reduce the number of hydroxyl groups via grafting reaction. Fig.5.c and Fig.5.d exhibit the similar dispersion state of silica. It can be conclude that the surface modification effect on silica of P-RT is not inferior to that of TESPT. After TESPT is used to modify P-RT, the hydroxyl concentration on the surface of P-RT reaches lower level and the polarity of P-RT gets weaker. Hence, the aggregations formed by P-RT become smaller, and the filler in NR/P-RT/TESPT composite demonstrates the best compatibility with NR matrix.

Reinforcement performance of P-RT on NR matrix

When the vulcanized NR without reinforcing filler is under stress action, the external stress will break the rubber molecular chains, and the continuous-strong stress action will contribute to the fraction of rubber composite. When NR is filled

with unmodified silica, the rubber molecule chains will form double rubber layers on the surface of silica because of the interaction between filler and rubber matrix [29, 30]. The microstructure of the double rubber layer is exhibited in Fig.6.a. In comparison to the unmodified silica, an organic layer consisting of coupling agent and grafted antioxidant forms on the surface of modified silica, which locates between the silica and bound rubber, as shown in Fig.6.b. The chain segments of the inner rubber layer lose their mobility on account of bonding with silica. The bound rubber fixed on the silica presents the same motion state as glassy state, but the molecular chains in the outer rubber layer can move freely. When the NR/silica composite suffers from continuous and strong stress action, the outer rubber layer first slides, and then the rubber molecular chain is broken. It is because the breaking energy is far greater than the energy needed for the sliding of rubber molecular chain [29-32].

Since the bound rubber plays an important role on reinforcing the rubber matrix, it is essential to determine the content of bound rubber in NR composites, and the results are listed in Table.3. It is obvious that the content of bound rubber in NR/P-RT/TESPT elastomer is the highest among the four kinds of NR elastomers, while the NR/silica/AO elastomer contains the lowest loading of bound rubber. Compared with the NR/silica/TESPT elastomer in which the content of bound rubber is 48.5%, the bound rubber content in NR/P-RT increases by 8%.

Chemical bonding and physical adsorption are two kinds of formation mechanisms of bound rubber. In NR/silica/AO and NR/P-RT composites, the physical

adsorption is the principal formation mechanism of bound rubber, and the chemical

bonding between silica and rubber molecules is negligible [33]. The amount of bound

rubber formed by physical adsorption depends on the interfacial interaction between

the silica and rubber matrix, and the stronger interface interaction is conducive to

form more bound rubber [29, 31]. It is apparent that the poorest compatibility

between the unmodified silica and NR matrix makes NR/silica/AO contain the lowest

content of bound rubber. Because the contents of silica in the four kinds of NR

composites are equal, low content of bound rubber means thin bound rubber layer

on the surface of silica. The organic layer on the surface of silica contributes to

strengthening the interfacial interaction between inorganic filler and organic rubber

matrix, and the thicker organic layer can attract more rubber molecular chains to

bond with the filler. In NR/silica/TESPT and NR/P-RT/TESPT composites, both the

chemical bonding and the physical adsorption can contribute to the formation of

bound rubber. Although there is no chemical bonding in NR/P-RT composite, the

large amount of grafted antioxidant can reduce the silanol groups on the surface of

silica and strengthen the interfacial interaction between the silica and rubber matrix,

increasing the amount of bound rubber formed by the strong physical adsorption.

Hence, the content of bound rubber in NR/P-RT/TESPT composite is far more than

that in the other three kinds of NR composites, because of the chemical bonding and

the strong physical adsorption between the silica and rubber matrix. Meanwhile, the

fact that NR/P-RT composite contains more bound rubber than NR/silica/TESPT

composite reveals that the P-RT of high grafting efficiency possesses much stronger

physical adsorption to rubber molecules than the silica modified by TESPT.

The affections of general silica and modified silica on the mechanical property of NR composites are mainly embodied in the variation of tensile strength and elongation at break of NR composites. The stress-strain curves of NR composites containing different kinds of fillers are presented in Fig.7, and the values of tensile strength of the NR composites are listed in Table.4. It is evident that the unmodified silica produces little reinforcement effect on NR matrix, and even the tensile strength appears a slight decrease. However, with the incorporation of P-RT (10 phr) into NR matrix, the tensile strength of NR/P-RT composite rises from 14.8 MPa to 20.1 MPa. After the precipitated silica is modified by TESPT of which the content is equal to the organic content in P-RT, the tensile strength of NR/silica/TESPT composite is 3.4 MPa more than that of pristine NR, but it is 1.9 MPa less than that of NR/P-RT composite. What's more, after an equal amount of TESPT is used to carry out the surface treatment for P-RT, the tensile strength of NR/P-RT/TESPT composite increases to 25.4 MPa. In addition, there is no big difference in the elongation at break of the five kinds of NR composites, meaning that the improvement of tensile strength of NR is not at the sacrifice of toughness of NR.

The content of bound rubber in NR composite is a key factor of determining the mechanical property of NR composite. When the NR composites are subjected to too strong stress action which can compel the rubber molecular chains to reach the maximum elongation, the rubber molecular chains in the outer layer first slide from the bound rubber, and then the strain energy is emitted as heat in this process,

avoiding the fracture of rubber molecular chains [29, 30]. The thicker the bound rubber layer is, the higher the sliding energy is. Although a small amount of bound rubber exists in NR/silica/AO composite, the large amount of large aggregations formed by unmodified silica partially break the network structure of NR matrix. The affection of large aggregations offsets the contribution of bound rubber to the improvement of mechanical property of NR matrix, so the incorporation of unmodified silica is not able to increase the tensile strength of NR matrix. Hence, the tensile strength of NR/silica/AO composites is the lowest among the five kinds of NR composites.

However, after the surface modification to silica, the reduction of silicon hydroxyl on the surface of silica improves the dispersity of silica in NR matrix, reducing the destructive effect of the aggregations on the cross-linking network of rubber. In NR/P-RT/TESPT composite, the high sliding energy resulting from the thick bound rubber layer enables more strain energy to be dissipated in the sliding process of rubber molecular chains. What's more important is that P-RT is chemically combined with the cross-linking network of NR matrix via TESPT, producing more close interaction between the P-RT and NR matrix. Therefore, the NR/P-RT/TESPT composite in which the rubber molecular chains need the highest strain energy for fracture possesses the highest tensile strength, and NR/silica/AO composite containing the lowest bound rubber content possesses the lowest tensile strength. Additionally, the similar bound rubber contents and dispersion states of modified silica in NR/P-RT and NR/silica/TESPT bring about the similar tensile strength of these

two kinds of NR composites.

Based on the above analysis, it can be concluded that the tensile strength of those five kinds of NR composites mainly depends on the content of bound rubber. In terms of the surface modification to silica, the surface modification efficiency of the modified silica in NR/P-RT/TESPT composite is the highest, and the surface modification efficiency of the grafted antioxidant is no less than that of traditional TESPT surface modifier.

The anti-oxidation efficiency of P-RT in NR matrix

The OIT test and accelerated aging test were carried out to estimate the thermal oxidation resistance of NR composites. OIT is the time interval between the initiation of oxygen flow and the onset of the oxidation of sample, which is commonly used to assess the stability of material and the anti-aging efficiency of antioxidant. The longer the OIT is, the better the thermal oxidation resistance of material is. The DSC curves of NR composites are showed in Fig.8, and the OIT values of those NR composites are presented in Table.5. It can be found that the OIT value of NR/silica composite is the shortest (8.3 min) among the five kinds of NR composites, and NR/P-RT composite possesses the longest OIT (55.8 min). The OIT value of NR/AO is 38.1 min which is three times as long as that of NR (12.7 min), but the OIT value of NR/silica/AO is only 24.4 min.

Because of the strong water-absorbing capacity of precipitated silica, the unmodified silica accelerates the diffusion rate of moisture into rubber matrix. In this humid condition, the degradation of rubber molecular chain surrounded by a great

deal of water molecules is induced easily [12]. Moreover, the unmodified silica has an accelerating effect on the thermal oxidation of rubber matrix, especially at high temperature [25, 34]. Therefore, the NR/silica shows the poorest thermal oxidation resistance. With the incorporation of antioxidant, the thermal oxidation resistance of NR/silica/AO is improved obviously.

As we know, the unmodified silica has strong adsorption to vulcanizing agent of low molecular weight, and the antioxidant 4010NA of low molecular weight is also easy to be absorbed by silica, reducing the anti-oxidation efficiency of 4010NA. Hence, without the negative effect of precipitated silica on anti-oxidation performance, the thermal oxidation resistance of NR/AO composite is much better than that of NR/silica/AO composite. In contrast with the NR/AO composite, NR/P-RT composite containing the same antioxidant content exhibits more outstanding anti-aging performance. It may be due to the volatilization of 4010NA during the processing and testing [35]. Since the thermal oxidation degradation of rubber molecular chain is very sensitive to the concentration of hydroxyl in rubber matrix, the feeblish water-absorbing capacity of P-RT resulting from the reduction of hydroxyl groups on the surface of P-RT leads to the improvement of anti-oxidation performance of SBR/P-RT composite.

In terms of evaluating the antioxidative efficiency of antioxidant, the service life of antioxidant also should be taken into consideration. In general, the service life of those antioxidants which are easy to migrate from rubber matrix to outside is short, and the migration rate of antioxidant can be investigated through the changes of OIT

of rubber composites upon solvent extraction, as shown in Fig.9. Although the initial OIT of NR/AO is quite long, it sharply declines with the extension of extraction time. After extraction for 24 hours, the OIT value of NR/AO reduces by 63% to 14.3 min, which indicates that 4010NA is able to migrate from NR matrix to the deionized water in a short time. The trend of the OIT value of NR/silica/AO is similar with that of NR/AO during the extraction experiment. Therefore, the service life of the low molecular weight antioxidant 4010NA in NR matrix is very short. On the contrary, even though the extraction time reaches up to 7 days, the OIT value of NR/P-RT composite still remain the 90% of its initial OIT value, showing the perdurability of the anti-oxidation effect of P-RT.

Investigating the changes of mechanical property of material during accelerated aging is another effective method to evaluate the anti-aging performance of material. The higher residual rate of mechanical property means more effective anti-aging performance of material. Fig.10 shows the change tendency of the tensile strength of NR composites during the accelerated aging at 85 ℃, and the residual rate of tensile strength is presented in Fig.11. In the process of accelerated aging, the residual rate of the tensile strength of NR/P-RT is always higher than that of the other NR composites. After aging for 12 days at 85 ℃, the tensile strength of NR/P-RT composite is 12.4 MPa, while the tensile strength of NR/silica/AO and NR/AO composite are only 7.6 MPa and 5.8 MPa, respectively. At the end of accelerated aging, the residual rate of NR/P-RT is the highest (60.6%) among these three kinds of NR composites, showing the preeminent anti-aging performance of P-RT.

The residual rates of the tensile strength of these three kinds of NR composites are almost the same in the first half of accelerated aging, but the gaps in the residual rate of tensile strength grow with the extension of aging time. It is apparent that the anti-aging effect of the blend system consisting of silica and 4010NA can't last long at high temperature, which results from the fugitiveness of 4010NA. When the NR composites are subjected to a short aging time, the volatilization rate of 4010NA is low. Once 4010NA begins to volatilize, a rapid reduction of the tensile strength of NR/silica/AO and NR/AO composites occurs. On the contrary, after 4010NA is fixed on the surface of silica, P-RT exhibits remarkable stability in NR matrix. Both the extraction experiments and accelerated aging tests demonstrate that the grafting method is effective to extend the service life of antioxidant.

To sum up, after being grafted onto the surface of silica, P-RT possesses more outstanding anti-aging performance and stability in contrast with the corresponding low molecular counterpart (4010NA), ensuring that P-RT can prevent the rubber matrix from aging for a long time.

Conclusions

In this paper, it has been confirmed that RT was successfully grafted onto the surface of precipitated silica via KH560, and the grafting efficiency of this sol method was high. This precipitated-silica-based immobile antioxidant exhibited good dispersion state in NR matrix. The excellent reinforcement performance of P-RT has demonstrated that the surface modification efficiency of this sol-grafting method is no less than that of the traditional surface modifier TESPT. It has been revealed that

this sol-grafting method can effectively enhance the anti-aging efficiency of antioxidant in NR matrix.

Acknowledgements

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Table.1 Composition of NR vulcanizates

Sample	NR	NR/silica/AO	NR/P-RT	NR/silica/TESPT	NR/silica	NR/AO	NR/P-RT/TESPT
NR	100	100	100	100	100	100	100
Silica	--	7.46	--	7.46	7.46	--	--
4010NA	--	1.23	--	--	--	1.23	--
P-RT	--	--	10	--	--	--	10
TESPT	--	--	--	2.82	--	--	2.82

Table.2 Composition of NR elastomer

Sample	NR/silica/AO	NR/P-RT	NR/silica/TESPT	NR/P-RT/TESPT
NR	100	100	100	100
silica	7.46	--	7.46	--
P-RT	--	10	--	10
4010NA	1.23	--	--	--
TESPT	--	--	2.82	2.82

Table.3 The content of bonding rubber in NR composites

Sample	NR/silica/AO	NR/P-RT	NR/silica/TESPT	NR/P-RT/TESPT
Bonding rubber (wt%)	28.2	57.5	51.3	69.7

Table.4 The tensile strength of NR composites

Sample	NR	NR/silica/AO	NR/P-RT	NR/silica/TESPT	NR/P-RT/TESPT
Tensile strength(MPa)	14.8	13.9	20.1	18.2	25.4

Table.5 The OIT values of NR composites

Sample	NR	NR/silica	NR/AO	NR/silica/AO	NR/P-RT
OIT(min)	12.7	8.3	38.1	24.4	55.8
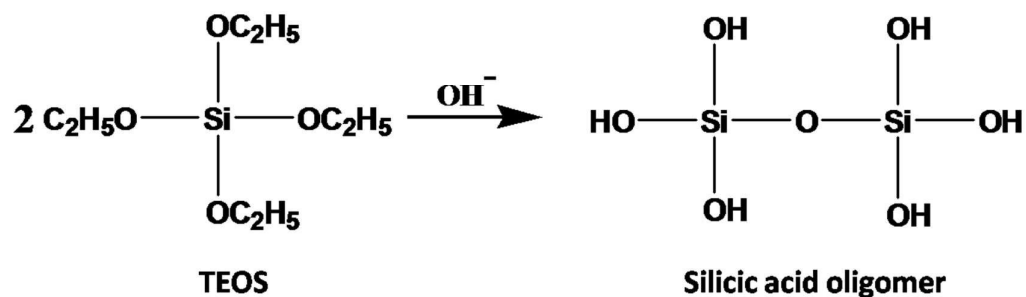
Fig.1 The hydrolysis reaction of forming silicic acid oligomer
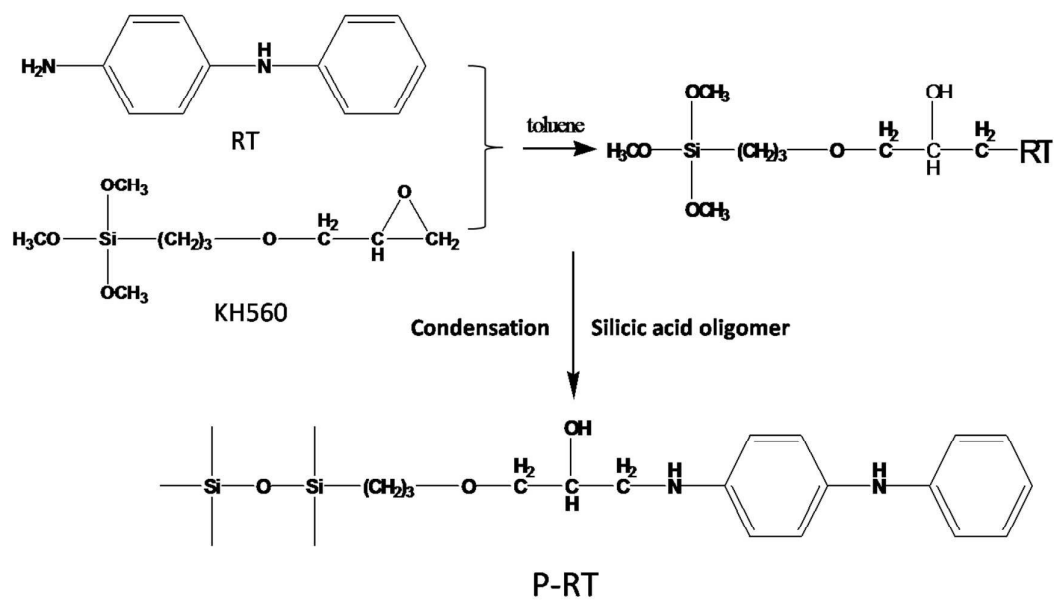
Fig.2 Synthesis of P-RT
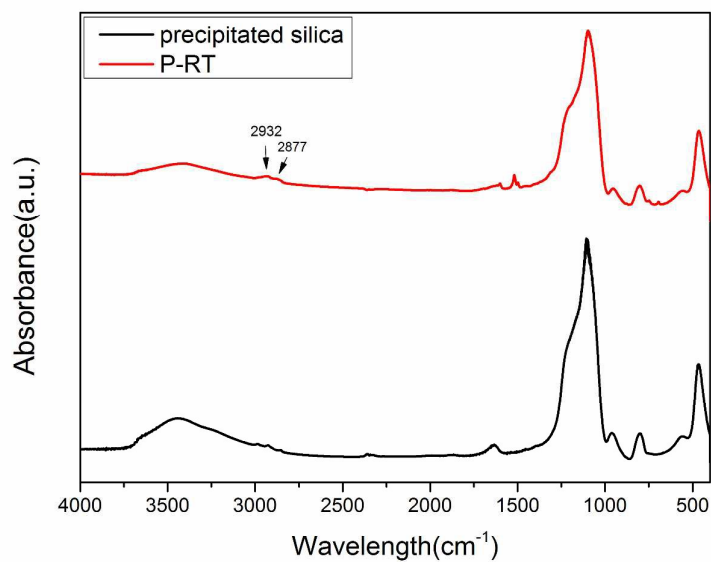
(a)
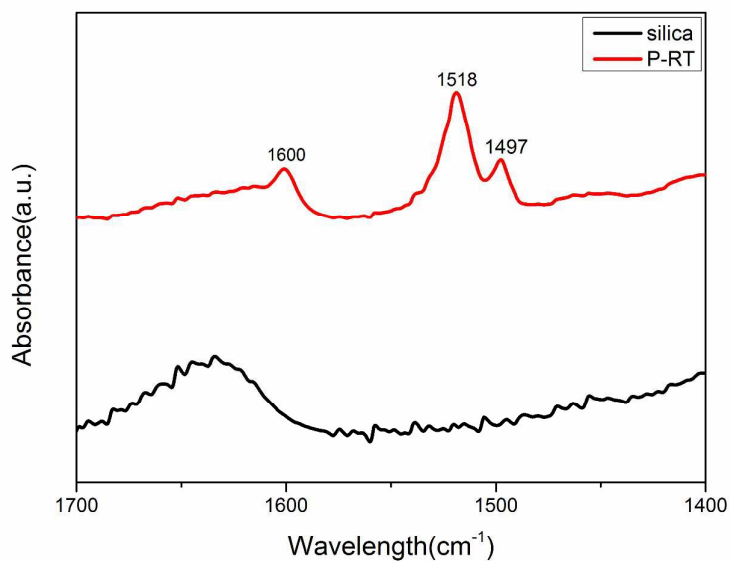
(b)

Fig.3 FTIR spectra of P-RT and precipitated silica (a) from 4000 to 400 cm^{-1} and (b) from 1700 to 1400 cm^{-1}.
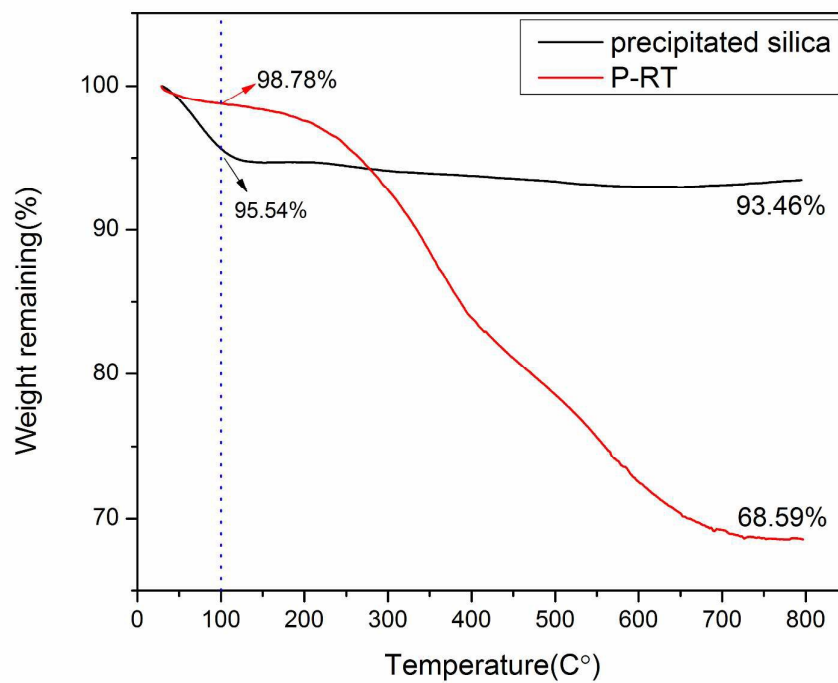

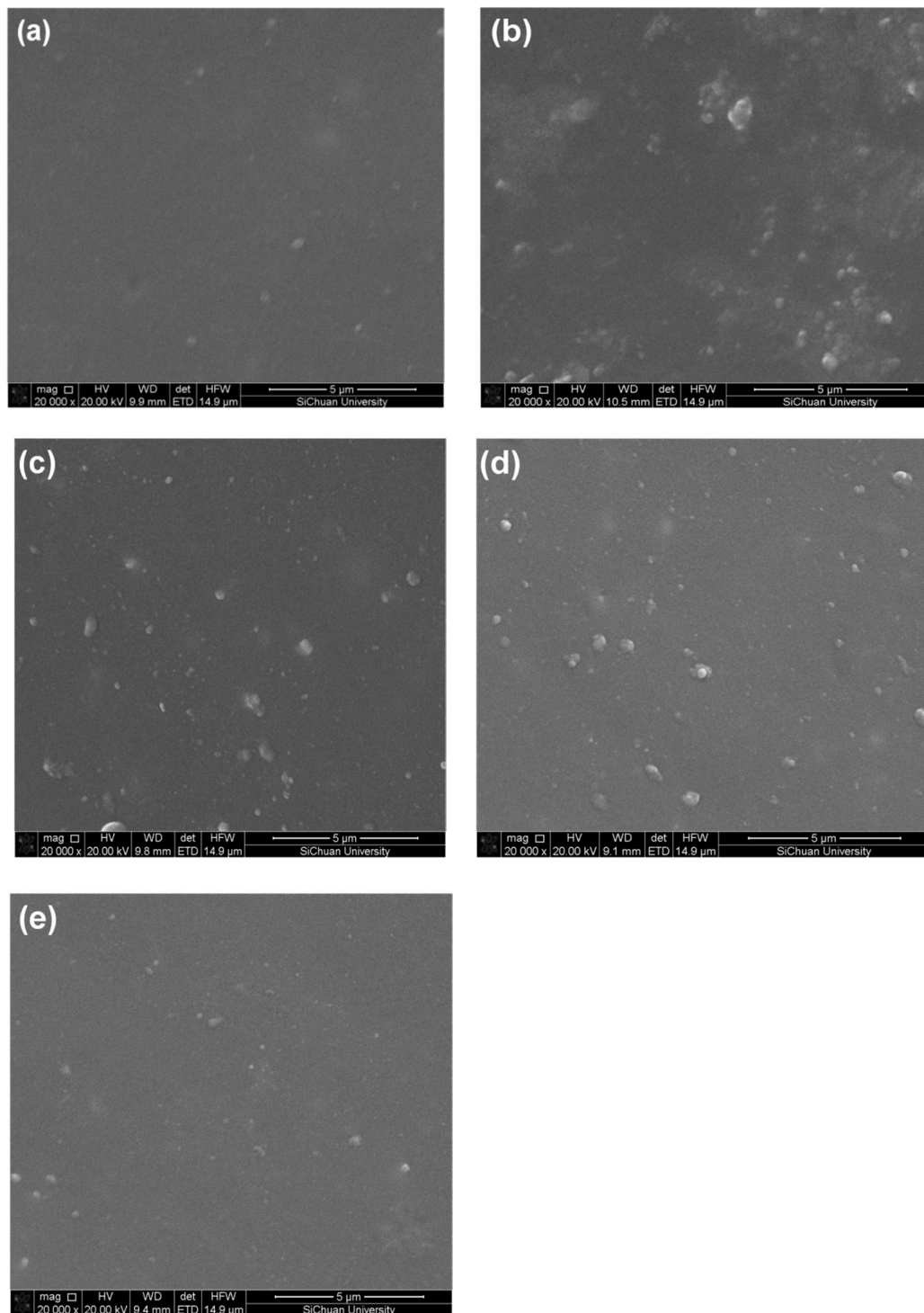Fig.4 TG curves of P-RT and precipitated silica

Fig.5 SEM images of (a) NR, (b) NR/silica/AO, (c) NR/P-RT, (d) NR/silica/TESPT and (e) NR/P-RT/TESPT
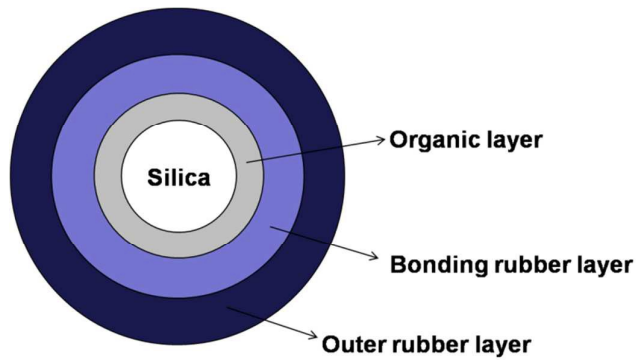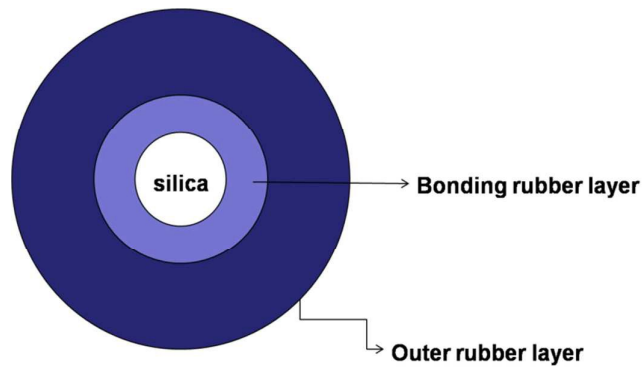
(a)

(b)

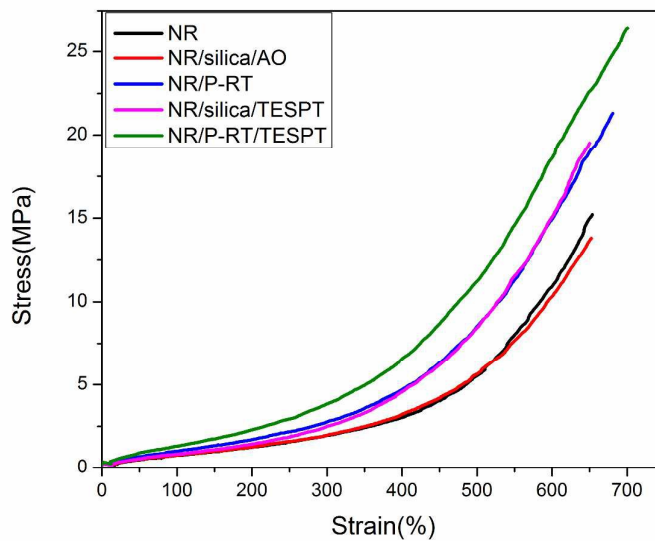Fig.6 Structure of double rubber layers on the surface of (a) unmodified silica and (b) modified silica
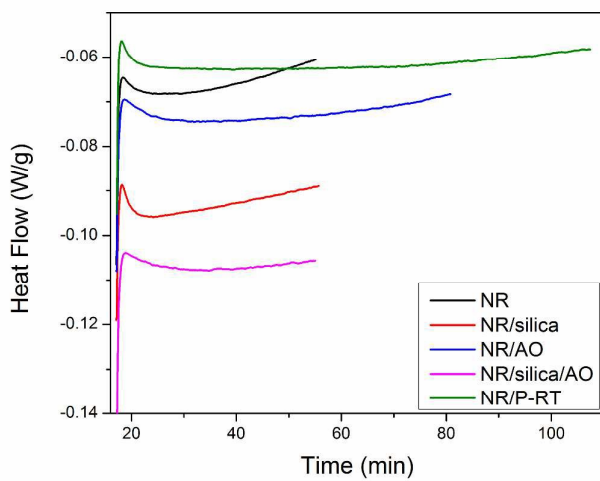
Fig.7 Stress curves of pristine NR and its composites
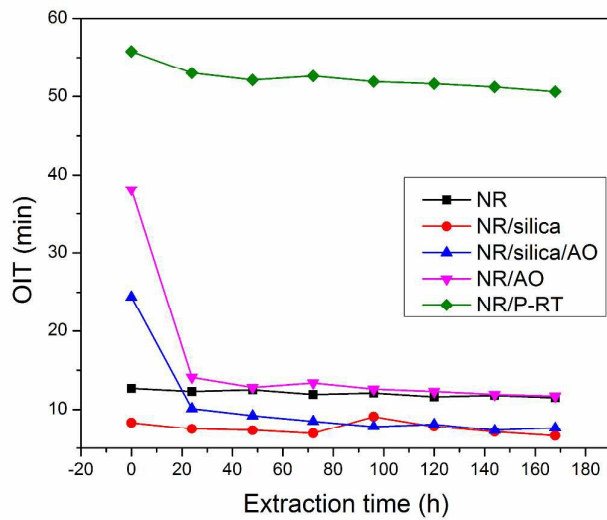

Fig.8 DSC curves of determining OIT

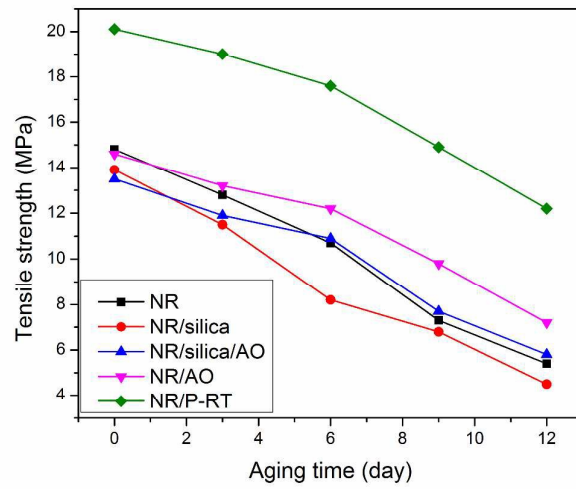

Fig.9 OIT versus extraction time of NR composites

Fig.10 The change of the tensile strength of NR composites during accelerated aging
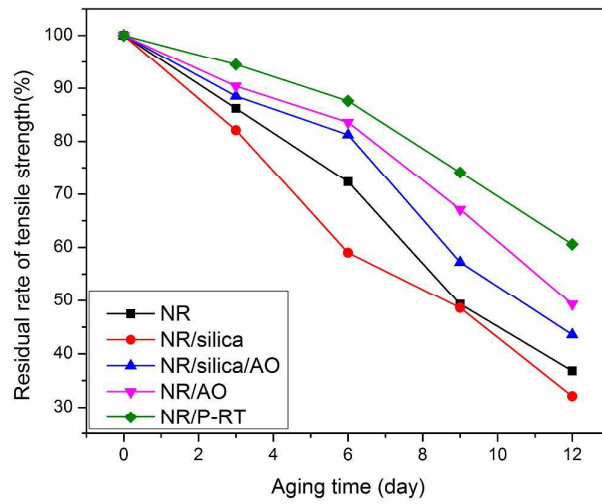

Fig.11 The change of the residual rate of tensile strength of NR composites during accelerated aging