

Synthesis and Aging Properties of Reactive Antioxidant NAPM in Natural Rubber Vulcanizates

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Received 28 February 2007; accepted 24 June 2007

DOI 10.1002/app.27042

Published online 7 January 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The rubber antioxidant *N*-(4-anilinophenyl) methacrylamide (NAPM) was synthesized by a two-step reaction using thionyl chloride (SOCl₂) with methacrylic acid (MAA) and consequently 4-aminodiphenylamine (ADPA) as precursors. NAPM was characterized by IR, ¹H NMR and elemental analysis. Thermal stability, aging property of NAPM and mechanical properties of natural rubber (NR) vulcanizates containing NAPM were investigated and compared with two other commercial antioxidants *N*-isopropyl-*N'*-phenyl-*p*-phenylene diamide (4010NA) and *N*-(1, 3-dimethyl butyl)-*N'*-phenyl-*p*-phenylene diamide (4020). It was found that NAPM was an

effective antioxidant with a better thermal stability and higher antiaging resistance than unreactive antioxidants 4010NA and 4020. And unsaturation level of NR vulcanizates containing NAPM was lower than that of 4010NA and 4020. Moreover, an antiaging resistant mechanism of a surface reaction between NAPM and *cis*-1, 4-polyisoprene in NR was proposed to explain the better properties of NAPM based on the IR and SEM analyses. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 576–582, 2008

Key words: antioxidants; rubber; degradation; mechanical properties; aging

INTRODUCTION

Because of the superior properties of NR, it is still necessary as a basic material for tires, latex gloves, condoms, seals, and many other things.^{1,2} Unfortunately, NR, a highly unsaturated rubber, degrades with time because of all kinds of aging.³ Degradation of NR very often limits its service lifetime,^{4–6} ultimately reaching to the point where NR is no longer able to fulfill its expected function safely.

Two main processes, thermal oxidation and ozonolysis initiate degradation of NR. The former is an autocatalytic, active free radical chain reaction where oxidation products are chiefly carboxylic acids, ketones, aldehydes, epoxides, etc. The presence of ozone in the atmosphere, even at a low concentrate, will be sufficient to cause degradation in NR due to the high reactivity of ozone with carbon–carbon double bonds in NR.³ Such degradation reaction by ozone results in chain scission and formation of polymeric peroxides, which yet will accelerate thermal oxidation.⁷

To prevent thermal oxidation and ozonolysis of NR, addition of antioxidants is one of the most convenient and effective methods since such addition will not change processing conditions.⁸ Apparently, such antioxidants are effective over long periods,⁹ in

other words, they should be involatile and unable to be leached out or removed from NR,^{9–10} which prompted us to develop such rubber antioxidants. Therefore, the strategy combining unsaturated methacryloyl chloride (MAC) with ADPA was applied to prepare the reactive antioxidant NAPM in this work.

Literatures on preparation and antiaging properties of the reactive antioxidant NAPM are scarce.¹¹ The present work was to provide an effective pathway for the synthesis of NAPM and to investigate its aging resistant and mechanical properties. Furthermore, comparisons between antiaging properties of NAPM and those of two other commercial antioxidants 4010NA, 4020 were carried out.

EXPERIMENTAL

Materials

NR was supplied kindly by the Dalian, JIN-HONG Rubber Ltd. Compounding ingredients, such as zinc oxide, stearic acid, carbon black, magnesium carbonate, calcium carbonate, light calcium carbonate, DM (dibenzothiazole disulfide), M (2-Mercaptobenzothiazole), D (diphenylguanidine), NOBS (*N*-Oxydiethylene-2-benzothiazole salphenamide), TS (Tetraethyl thiuram monosulfide), petroleum resin, and sulfur, are of commercial grade. MAA, aniline, SOCl₂ (thionyl chloride), hydroquinone, Potassium iodide, Sodium thiosulfate pentahydrate, sodium chloride,

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TABLE I
Elemental Analysis of NAPM

| | C | H | N | O |
|----------------|------|-----|------|-----|
| Found (%) | 76.1 | 6.3 | 11.3 | 6.3 |
| Calculated (%) | 76.2 | 6.3 | 11.1 | 6.4 |

ADPA, Carbon bisulfide, used for synthesis and iodometry studies are of reagent grade.

Preparation of NAPM

The antioxidant NAPM was prepared by a two-step process as follows.

SOCl_2 was added to MAA dropwise with a molar ratio of SOCl_2/MAA 1.5 : 1 at 10°C . With a little amount of hydroquinone as retarder, the mixture was heated from 25 to 60°C with a heating rate of 10°C h^{-1} . In this case, the intermediate MAC was obtained with the high yield of 88.6%. Secondly, into a three-necked flask equipped with a condenser and an addition funnel, 9.212 g (0.05 mol) ADPA and 20 mL anhydrous ether were added with stirring under nitrogen. Then the mixture was cooled with ice bath to 0°C , 4.52 g (0.0525 mol) MAC was added dropwise, and 4.656 g aniline was added. After 20 min, the temperature was slowly raised to 25°C and maintained for 3 h with the solution turning to saffron yellow. Upon removal of the solvent, a light yellow powder was obtained. The crude product was purified from recrystallization in *p*-xylene. After

TABLE II
Recipe Used for NR Blends

| Ingredients | Amount (phr ^a) | | |
|-------------------------|----------------------------|------|------|
| | | | |
| NR | 100 | 100 | 100 |
| Zinc oxide | 5 | 5 | 5 |
| Stearic acid | 0.3 | 0.3 | 0.3 |
| Magnesium carbonate | 15 | 15 | 15 |
| Calcium carbonate | 27.5 | 27.5 | 27.5 |
| Light calcium carbonate | 25 | 25 | 25 |
| DM ^b | 0.35 | 0.35 | 0.35 |
| M ^c | 0.1 | 0.1 | 0.1 |
| D ^d | 0.2 | 0.2 | 0.2 |
| NOBS ^e | 0.9 | 0.9 | 0.9 |
| TS ^f | 0.05 | 0.05 | 0.05 |
| petroleum resin | 0.3 | 0.3 | 0.3 |
| carbon black | 0.3 | 0.3 | 0.3 |
| Sulfur | 2.35 | 2.35 | 2.35 |
| Antioxidant 4010NA | 1 | – | – |
| Antioxidant 4020 | – | 1 | – |
| Antioxidant NAPM | – | – | 1 |

^a phr, parts per hundred.

^b Dibenzothiazole disulfide.

^c 2-Mercaptobenzothiazole.

^d Diphenyl guanidine.

^e N-Oxydiethylene-2-benzothiazole salphenamide.

^f Tetramethyl thiuram monosulfide.

dried in a vacuum oven at room temperature for 72 h, a flaxen powder product was produced. Yield: (76.53%) M.p.: $100\text{--}106^\circ\text{C}$. ^1H NMR (500 MHz, CDCl_3), d: 6.4–7.5(m, Ar–H), 5.4(s, Ar–N–H), 7.45(s, CON–H), 5.5, 5.9(d, =CH₃), 2.06 (s, O=C–C–CH₃). IR (KBr), 1653.9 cm^{-1} (str, C=O); 3358.2 cm^{-1} , 1604.0 cm^{-1} (str, N–H); 2975.9 cm^{-1} (str, –CH₃); 815.7 cm^{-1} , 744.4 cm^{-1} (phenyl ring); 1522.1 cm^{-1} (str, ARN–H). The result of elemental analysis of this product was listed in Table I.

Characterization and property evaluation

IR spectroscopy

Infrared spectrophotometry (IR) spectra were recorded on a Fourier-transform infrared spectrometer (Thermo Nicolet Nexus) in KBr discs.

NMR measurement

Proton NMR spectra were measured in deuterated CH_2Cl_2 containing tetramethyl silane as an internal standard and recorded on a Varian INOVA –400-MHz NMR spectrometer.

Elemental analysis

The elemental analysis was determined with an elemental analyzer (vario EL III, elemental instrument, Germany). The specimen was heated in a helium environment with a flow rate of 200 mL/min.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) of NR specimens were performed with a Mettler-Toledo SDT851e Thermo-balance controlled by a PC under the Win-

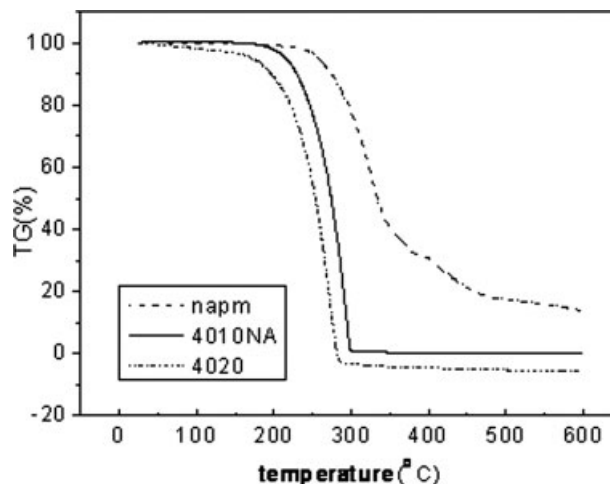


Figure 1 TG curves of the antioxidants NAPM, 4010NA and 4020.

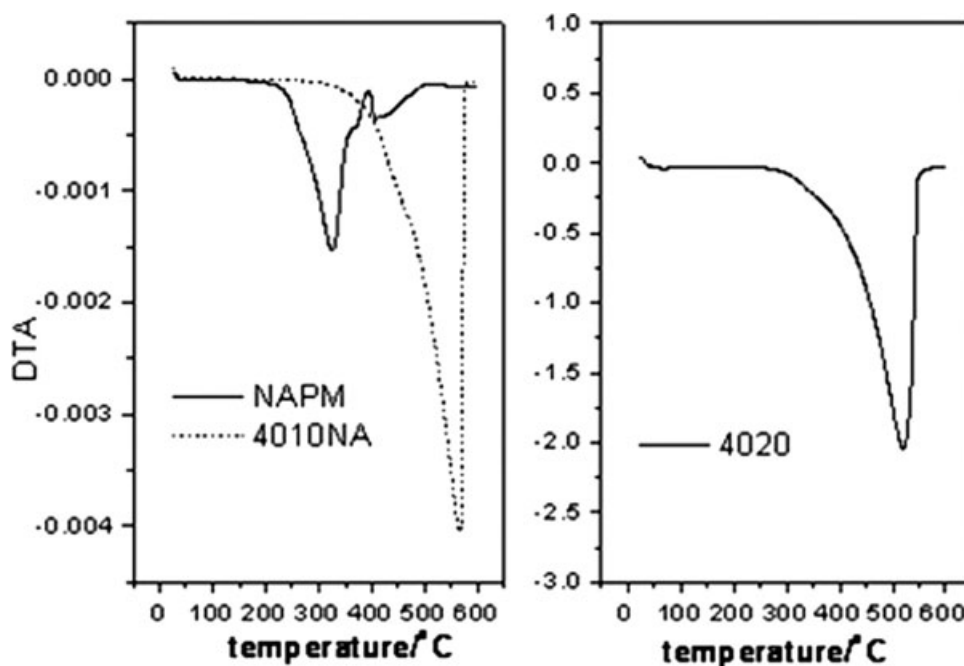


Figure 2 DTG cures of the antioxidants NAPM, 4010NA and 4020.

dows operating system. The tests were carried out in a nitrogen environment with a flow rate of 70 mL/min. Samples of 5 mg were heated at the rate of 10 K/min from 298 to 873 K.

SEM analysis

To investigate the configuration of NR vulcanizates specimens, characterization of Scanning Electron Microscopy (SEM) was carried out with a KYKY-2800B scanning electron microscope.

Unsaturation level measurement

Unsaturation level of NR vulcanizates was established by iodometry.¹² The procedure was as follows:

After extracting in acetone/petroleum ether with the ratio of 3/1 in volume, the NR specimens were kept at 50°C in a vacuum oven until the weight of the specimens did not decrease. A total of 0.1000 g specimen and 75 mL carbon bisulfide were added into a 500 mL brown flask then kept static over night. Twenty-five milliliter self-prepared acetum

dissolved iodine chloride was added with shake up. After being kept in dark for one hour, 25 mL 15% of kalium iodide solution and 50 mL fresh distilled water was added to the mixture. Subsequently, the mixture was subjected to titration with the standard 0.05 mol/L sodium hyposulfite solution. When the mixture was straw yellow, 5 mL 1% amyllum solution was added as indicator, continuing to titrate until the blue color disappeared. At the same time, the blank tests were also done.

Mechanical properties tests

All samples were made from unsaturated NR, as more NR was consumed annually than synthetic rubber.¹³ The recipe used is listed in Table II. Isoprene rubber was first masticated for 2 min before charging stearic acid or antioxidant. Mixing was further carried out for 6 min by a mixer typed XK-160. Subsequently, the other ingredients were added and mixed for 10 min. The mixture was sheeted on a mill keeping at room temperature for 24 h before testing. Rubber samples were preheated for 1 min at 125°C, Mooney viscosity (ML (1 + 4) – 125°C) of

TABLE III
The Detailed Datum for TGA

| Antioxidants | Temperature range/°C | Onset temperature/°C | Peak temperature/°C | T_{max} /°C |
|--------------|----------------------|----------------------|---------------------|---------------|
| NAPM | 100–600 | 260 | 325 | 600 |
| 4010NA | 100–600 | 220 | 300 | 300 |
| 4020 | 100–600 | 200 | 280 | 280 |

TABLE IV
Mechanical Properties of NR Vulcanizates Containing Different Antioxidants Before and After Aging

| | | NAPM | 4010NA | 4020 |
|--|---|--------|--------|--------|
| ML (1 + 4) – 125/°C Rheometer cure data | ML/min | 3.75 | 3.69 | 3.62 |
| | F_L /NM | 0.148 | 0.179 | 0.16 |
| | F_{max} /NM | 1.101 | 1.136 | 1.112 |
| | t_{50} /min | 2.05 | 2.14 | 2.24 |
| | t_{90} /min | 3.03 | 3.18 | 3.27 |
| Normal physical properties | Tensile strength(σ_{break})/MPa | 16.38 | 17.55 | 16.05 |
| | Elongation at break(ϵ_{break})/% | 596.6 | 622.83 | 623.8 |
| | Hardness | 50 | 47 | 48 |
| The physical properties after 70°C × 48 h aging | Tensile strength(σ_{break})/MPa | 16.08 | 17.33 | 16.07 |
| | Elongation at break(ϵ_{break})/% | 589 | 615.3 | 614.75 |
| | Hardness | 49 | 46 | 46 |
| Aging coefficient (K) after 70°C × 48 h aging The physical properties after 70°C × 72 h aging | | 0.9692 | 0.9755 | 0.9717 |
| | Tensile strength(σ_{break})/MPa | 15.99 | 15.83 | 15.06 |
| | Elongation at break(ϵ_{break})/% | 583.75 | 580.75 | 574.25 |
| Aging coefficient (K) after 70°C × 72 h aging | Hardness | 48 | 45 | 44 |
| | | 0.9552 | 0.8411 | 0.8638 |
| | | | | |

NR containing different antioxidants was obtained, respectively. Cure parameters were measured using a Mooney viscometer typed ZND-1 and a Rubber Process Analyzer at the test temperature of 125°C. Mooney scorch time (t_5) and the optimum cure time (t_{90}) were recorded. The mixture was then molded at 150°C according to each cure time determined by a rotor rheometer type MDR-2000. Dumbbells shaped tensile specimens were punched from a compression-molded slab along the mill grain direction. Five of these specimens were further aged in hot air at 70°C (for 24 h and 48 h) at each single. Aging has been carried out using an Aging Oven typed 401A (normal oven method with air circulation). Tensile strength and elongation at break were measured utilizing an Electron Tensile Testing Machine typed

DXLL-2500. The hardness of the specimen was determined by means of a Shore Hardness Tester typed XY-1.

RESULTS AND DISCUSSION

Thermal properties of antioxidants

In Figures 1 and 2 is given the TG and DTG curves of thermal degradation of the three different antioxidants in nitrogen, respectively. Table III shows the same results with them. It could be seen that the TG curves of these antioxidants show a single mass loss stage. However, on the DTG curve (Fig. 2), there is only one peak for 4010NA and 4020; whereas, there are two peaks for NAPM, indicating that the thermal degradations of 4010NA and 4020 in nitrogen were simple and were one-step reactions and that of

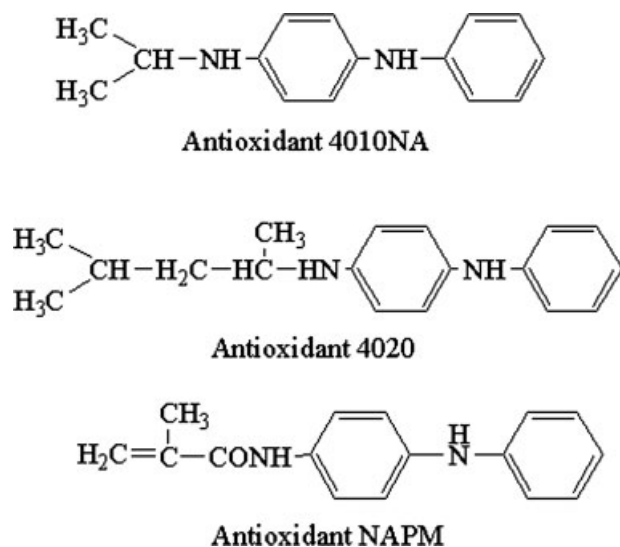


Figure 3 Structure of the antioxidants NAPM, 4010NA, 4020.

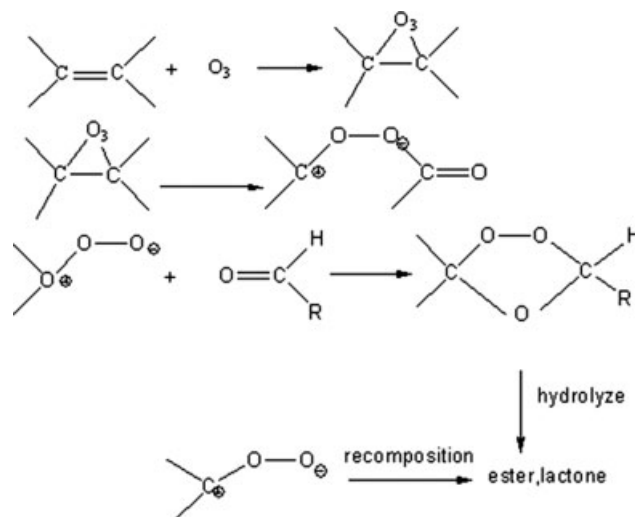


Figure 4 The mechanism of ozone oxidation.

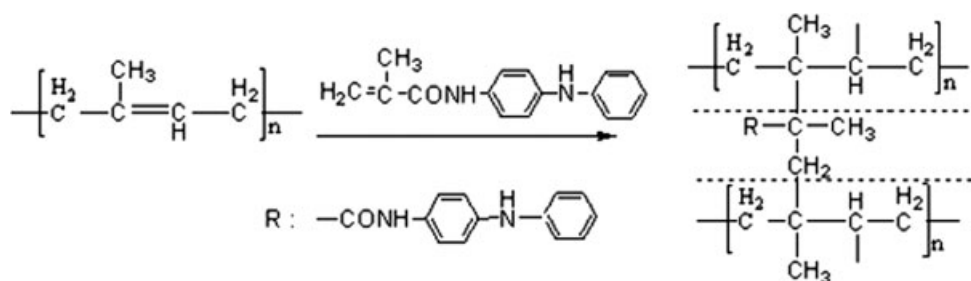


Figure 5 Schematic of the reaction between NR and NAPM.

NAPM is a more complicated one. Although, both TG and DTG curves shifted toward high temperatures along with the rising of the heating rate and the trends seen in the TG and DTG curves of the three different antioxidants were similar, the degradation started at about 160°C for 4010NA and 4020 and it was 240°C for NAPM. Moreover, 4010NA and 4020 left a residue at about 350°C, whereas it was at about 600°C for NAPM and in addition the residual mass has also been increased from 0% for 4010NA, 4020 and to 13% for NAPM. This indicated that the thermal stability of NAPM was higher than that of 4010NA and 4020, which was further substantiated by the peak temperature and T_{max} summarized in Table III.

Mechanical properties of NR vulcanizates

Table IV presents mechanical properties of NR vulcanizates containing different antioxidants before and after aging. Properties such as tensile strength (σ_{break}), hardness, and elongation at break ($\varepsilon_{\text{break}}$) were listed in Table IV. Herein, the aging coefficient was calculated as follows:

$$K = \frac{f}{f_0} \quad (1)$$

$$f = \sigma_{\text{break}} * \varepsilon_{\text{break}} \quad (2)$$

where, f_0 and f were the performance test values before and after aging, respectively. The eqs. (1) and (2) are empirical equations in the aging coefficient calculation. Table IV addresses that the gained aging coefficient (K) of NAPM equal to 0.9692 was slightly smaller than 0.9755 for 4010NA and 0.9717 for 4020 after 70°C × 48 h aging; nevertheless, it is markedly higher than that of 4010NA and 4020 after 70°C × 72 h aging, namely, $K(\text{NAPM}) > K(4020) > K(4010\text{NA})$, as is illustrated in Table IV. Hence, it could be concluded that aging resistance property of NAPM increased with the aging time while for 4010NA and 4020 did not. Thus, NR products containing NAPM would have longer service lifetime

than those of the other two. In addition, it is worth noting that in Table IV the hardness of NR vulcanizates containing NAPM was slightly larger than that of the other two antioxidants, thus indicating a slightly higher hardness for NAPM. To our knowledge, NAPM has the similar chemical structure as 4010NA and 4020; however, the main difference between them was that there were carbon-carbon double bonds ($\text{C}=\text{C}$) existing in NAPM but not in 4010NA and 4020 (Fig. 3). The double bonds ($\text{C}=\text{C}$) could chemically combine with NR by a surface reaction or react with ozone that had a high reactivity with carbon-carbon double bonds (Fig. 4), which would make the aging coefficient of NAPM higher.

Unsaturation level of NR vulcanizates

Unsaturation level of NR vulcanizates containing different antioxidants was measured by iodometry, as noted above (Section Characterization and property evaluation). Unsaturation level of NR vulcanizates containing NAPM decreased by 3.7, while that of 4010NA decreased by 3.1 during the process of vulcanization. Thus NR vulcanizates containing NAPM will have lower unsaturation level than 4010NA.

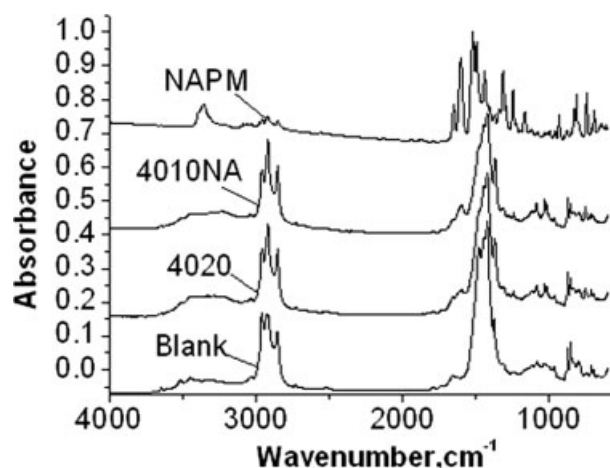


Figure 6 IR spectra of NR vulcanizates containing antioxidants 4010NA, 4020, NAPM and blank.

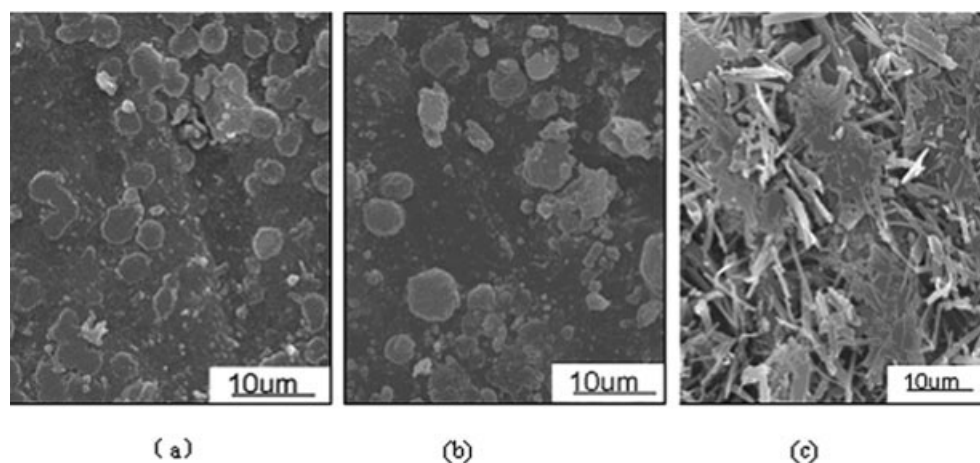


Figure 7 SEM images of NR vulcanizates with different antioxidants.

The proposed aging resistant mechanism of NAPM to NR

In above, it can be seen that the better thermal stability and aging resistant property for NAPM and the lower unsaturation level of NR vulcanizates containing NAPM were obtained, suggesting that NAPM is an effective aging resistant additive to NR. A reaction mechanism is proposed to explain these favorable properties as shown in Figure 5. Considering the carbon-carbon double bonds existing in NAPM, a surface reaction between NAPM and *cis*-1, 4-polyisoprene in NR takes place and is responsible for the better resistant and antiaging properties of NAPM.

In Figure 6 where IR spectra of NR vulcanizates containing antioxidants 4010NA, 4020, NAPM, and blank ones are showed, the absorptions of NR vulcanizates containing antioxidants 4010NA, 4020, and NAPM were somewhat similar to that of the blank one. Nevertheless, for the NR vulcanizates containing NAPM, the absorption around 3000 cm^{-1} was weaker than all the others, probably resulting from the surface reaction between NAPM and *cis*-1, 4-polyisoprene, which content is 93–95% in NR.¹³ And furthermore, looking at Figure 7(a,b,c) which show the SEM photos of surface morphologies of NR vulcanizates containing antioxidants 4020, 4010NA, and NAPM after $70^{\circ}\text{C} \times 48\text{ h}$ aging, respectively, a network structure was observed for NAPM while for 4010NA, 4020 the separate particles are distributed on their surface. The reason for formation of the network structure is considered that NAPM particles crosslinked with NR due to the surface reaction. Such surface reaction could result in lower unsaturation level of NR vulcanizates containing NAPM. Lower unsaturation level reasonably reduces the possibility of thermal oxidation and ozonolysis, favorably giving a higher aging coefficient and better thermal stability of NAPM. All the evidences above

support that NAPM is a reactive antioxidant really, and would not tend to leach out in process or its service life.

CONCLUSIONS

The rubber antioxidant NAPM was synthesized successfully by a two-step reaction using thionyl chloride (SOCl_2) with methacrylic acid (MAA) and consequently 4-aminodiphenylamine (ADPA) as precursors. NAPM was characterized by IR, ^1H NMR and elemental analysis. Thermal stability, antiaging property of NAPM, and mechanical properties of NR vulcanizates containing NAPM were investigated and compared with two other commercial antioxidants 4010NA and 4020. The followings are the results obtained:

- (1) NAPM has a good thermal stability;
- (2) As the aging time increases, NAPM has better aging resistance than unreactive 4010NA and 4020 with aging coefficients of 0.9552, 0.8411, and 0.8638, respectively;
- (3) Unsaturation level of NR containing NAPM was lower than that of 4010NA and 4020.

Based on IR and SEM analyses, an aging resistant mechanism of a surface reaction between NAPM and *cis*-1, 4-polyisoprene in NR is proposed to explain the better properties of NAPM as an aging resistant antioxidant to NR. The reactive antioxidant NAPM is an effective antioxidant to unsaturated rubber NR. The extended application of NAPM to other unsaturated rubber is also expected.

The authors would like to thank the companies who have supplied many free materials for the project; antioxidants 4010NA and 4020 from the Shen Ao Chemical engineering stock company, Shandong, China, natural rubber, accelerators and curing agents were supplied by JIN-HONG Rubber Ltd., Dalian China.

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