

Effect of Weight Ratio of Thermoplastic and Thermosetting Boron-Containing Phenolic Resin on Mechanical, Bonding, and Ablative Properties of Thermal Insulating Composites

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ABSTRACT: To improve the tensile strength, the bond strength, and the ablation resistant properties as well as the elongation at break of the short aramid fibers reinforced EPDM-based thermal insulation composites, two kinds of boron-containing phenolic resin, thermoplastic (TPBPR) and thermosetting (TSBPR), were added into the composites with a series of weight ratio of TPBPR and TSBPR, such as 0 : 20, 5 : 15, 10 : 10, 15 : 5, and 20 : 0. The effects of TPBPR and TSBPR weight ratio on the mechanical, bonding, and ablative properties of the composites were investigated systematically, respectively. The results showed that the crosslink density, the tensile strength, the bond strength, and the ablation resistant abilities of the

composites decrease continuously with the increasing weight ratio, which confirms that the mechanical reinforcement and the ablation resistant abilities of TSBPR are higher than that of TPBPR. However, the elongation increases sharply with TPBPR and TSBPR weight ratio increasing. Therefore, the optimal weight ratio of TPBPR and TSBPR should be 10 : 10 to obtain the very thermal insulation composites with the excellent comprehensive properties. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 266–274, 2010

Key words: composites; high performance polymers; resins; thermal properties

INTRODUCTION

The thermal insulating composites, located between the solid propellant and the metallic chamber, are the high-performance subsidiary component of the rocket motor. During the motor flying, the composites have to undergo the violent thermochemical ablation and thermomechanical erosion from the combustion gas with the temperature of above 3000°C and the speed of about 5 Mach,^{1,2} which requires the thermal insulation composites must own excellent ablation resistant properties. In addition, huge dimension deformation of the chamber and the solid propellant happens inevitably during the motor charging, transporting, storing, and flying. Thus, a big elongation at break is especially required to release this deformation, too.³ In other words, the ablative rates and the elongation at break are two key indexes for these composites to evaluate their properties.^{4–6}

Phenolic resin with short aramid fibers or short polyacrylonitrile (PAN) fibers has been introduced into the rubber matrix successfully to improve the ablation resistant properties of the thermal insulation composites since 1972 for its good thermal stability, excellent flame resistance, and outstanding mechanical properties.^{7,8} However, with the quick development of advanced rocket motor, the thermomechanical erosion and thermochemical ablation of the combustion gas flow on the phenolic resin reinforced rubber composites become more and more violent. As a result, the thermal and flame resistances of phenolic resin become too poor to meet the advanced rocket motor.⁹ Therefore, a series of modified phenolic resin has been reported by introducing boron element,^{10–12} molybdenum element,^{13,14} or aromatic ring,¹⁵ etc., in the molecule of phenolic resin to improve its thermal stability and flame resistance. Unfortunately, only the thermosetting boron modified phenolic resin (TSBPR) has been used widely in the thermal insulation composites or C/C composites for its higher thermal stability, higher carbon residue, and lower cost than other modified phenolic resins. In addition, our previous studies indicated when the content of TSBPR was 20 phr, the ablation resistant properties of short aramid fibers/ethylene-

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TABLE I
The Detailed Formula of the Composites (phr)

Components	C0/20	C5/15	C10/10	C15/5	C20/0
EPDM	100	100	100	100	100
DCP	4	4	4	4	4
Chloroparaffin	10	10	10	10	10
Antimony trioxide	5	5	5	5	5
Fumed silica	20	20	20	20	20
Aramid fiber (5 mm long)	8	8	8	8	8
TPBPR	0	5	10	15	20
TSBPR	20	15	10	5	0

phr is the parts by weight per 100 parts by weight of rubber.

propylene-diene-terpolymer (EPDM) composites became very excellent.^{16,17} The elongation at break of the composites was affected badly by the resin dosage. Furthermore, many studies reveal that the TSBPR reinforced composites will be further cured slowly to enhance the crosslink network of the vulcanized composites even at room temperature. As a result, the elongation of the composites reduces so sharply that it hardly meets the need of advanced rocket motor after being stored more than one year.¹⁶ Obviously, it is very disadvantage for the application of the very insulation composites on the advanced rocket motor.

Recently, Zhang⁹ added the thermoplastic boron-containing phenolic resin (TPBPR) into the pure acrylonitrile-butadiene rubber matrix. Dramatically, his results indicated that the elongation of the rubber hardly reduces with the dosage of TPBPR increasing. This promotes us to add this resin into the insulation composites to obtain huge elongation instead of reducing their ablation resistant abilities.

Therefore, in this research, TPBPR and TSBPR were both added into the short aramid fiber reinforced EPDM-based thermal insulating composites with the different weight ratio, such as 0 : 20, 5 : 15, 10 : 10, 15 : 5, and 20 : 0. The effects of TPBPR and TSBPR weight ratio on the mechanical, bonding, and ablative properties of the composites were investigated completely.

EXPERIMENTAL PART

Materials and specimen preparation

TPBPR (pink powder, sieved with 200 meshes, M_n : 1100–1200) and TSBPR (yellow massive solid, M_n : about 400) used in this study were provided by Xi'an Taihang Fire Retardant Plant. The weight ratios of TPBPR and TSBPR are 0 : 20, 5 : 15, 10 : 10, 15 : 5, and 20 : 0, respectively, with a total weight of 20 phr. Then the boron phenolic resins mixture and short aramid fibers (Twaron1001, Akzo Co., Holland) with 12 μm in diameter and 5 mm in length were added into EPDM matrix (EPDM4045, Jilin

chemical Co., China) by blending fumed silica, flame retardants (chloroparaffin and antimony trioxide), and vulcanization agent (dicumyl peroxide (DCP, Shanghai Fangruida Co., China)) in a two-roll mill. The detailed formula was listed in Table I. Except EPDM and aramid fiber belonging to commercial grade, other additives used in this study are all chemical grade.

After all the additives and short fibers were well dispersed in the rubber matrix on an usual two-roll mill for about 20 min, the unvulcanized composites were made into the tensile samples with 2 mm in thickness, the bonding samples with 4 mm in thickness and 25 mm in diameter, and the cylindrical ablation samples with 7 mm in thickness and 30 mm in diameter along the direction of machine rolling, respectively. Moreover, to study the effects of TPBPR and TSBPR weight ratio on the mechanical, bonding, and ablative properties of the EPDM-based thermal insulating composites, all the samples were vulcanized at 160°C and 15 MPa for 50 min while their vulcanization times (t_{90}) are different each other.

Measurements

Infra-red analysis and vulcanization behavior

A Fourier transform infra-red (FTIR) spectrometer was used to analyze the structure difference of TPBPR and TSBPR.

After boron phenolic resins and other additives were well dispersed in the EPDM matrix, the mixture was made into cylindrical sample with 40 mm in diameter and 4 mm in thickness and then was put into the cavity of MDR-2000 Rotorless Curemeter (Shanghai D&G measure instrument Co.) controlled by a computer to measure the vulcanization behavior at 160°C and 5 MPa according to ASTM D5289-07. At high temperature and high pressure, peroxide (DCP) could initiate the crosslinking of rubber compound to make the crosslink network and the viscosity of rubber mixture improved gradually. Accordingly, the cavity torque will increase

gradually with the vulcanization time increasing until the vulcanization process completes. The torques, including that at the vulcanization initial stage (ML) and that at the maximum values (MH), are detected by a computer. As a result, the vulcanization time (t_{90}) where its torque amounts to 0.9 (MH – ML) can be calculated quickly.

Thermal analysis

The thermogravimetric analysis (TG) and the differential thermogravimetric curves (DTG) of TSBPR and TPBPR were conducted on a thermogravimetric analyzer (Q1000DSC+LNCS+FACS Q600SDT, TA Co., America) from 20 to 800°C at 20°C/min in nitrogen atmosphere with N₂ flow rate of 40 mL/min. Moreover, the differential scanning calorimeter (DSC) was conducted from 20 to 200°C at 20°C/min in nitrogen atmosphere.

Crosslinking density of the vulcanization

The crosslinking density was determined by the equilibrium swelling. After vulcanized, the insulation samples with a dimension of 10 mm × 10 mm × 2 mm were swollen in toluene at 25°C for 96 h until the specimen weight did not change anymore. The weight of the samples was measured after fully swollen. Then the samples were dried in a vacuum oven at 90°C for 36 h and reweighed. The volume fraction of rubber swollen in the gel, V_r , which was used to represent the crosslink density of the vulcanizates, was determined by the following equation:

$$V_r = \frac{m_0\phi(1-\alpha)\rho_r^{-1}}{m_0\phi(1-\alpha)\rho_r^{-1} + (m_1 - m_2)\rho_s^{-1}} \quad (1)$$

where m_0 is the sample mass before swollen, m_1 and m_2 are the swollen sample masses before and after dried, respectively, ϕ is the mass fraction of EPDM rubber in the vulcanizates, α is the mass loss of the vulcanizates after swollen, and ρ_r and ρ_s are the rubber and solvent density, respectively.

Mechanical and bonding properties test

The mechanical properties tests were carried out on a CMT6503 tensile electron machine at a crosshead speed of 100 mm/min along the machine rolling direction according to ASTM D3039. Then the fracture morphology was observed on a scanning electron microscope (SEM, JSM-7600F, Japan).

Before carrying out the bonding property test, the unvulcanized composites were cut into test pieces about 25 mm in diameter and 4 mm in thickness. Then the test piece was placed into two 1045 plates pretreated with 120 sand papers and acetone and

then covered with the chemlok-205 adhesive (Load chemical Co., America). After vulcanized at 160°C and 15 MPa for 55 min, the bonding samples were disjoined on the CMT6503 tensile electron machine with the crosshead speed of 50 mm/min according to ASTM D2919-01.

Ablative properties test

To evaluate the ablative properties of the insulation composites, an oxyacetylene flame test was carried out according to ASTM E285-80 (2002) in this research. The erosion velocity of the hot combustion gas was controlled by the flow rate and pressure of acetylene (1116 L/h and 0.095 MPa) and oxygen (1512 L/h and 0.4 MPa), respectively. The vulcanized sample was fastened on a plate and the oxyacetylene flame was burst onto the center of the cylindrical specimen surface. The distance between the specimen surface and the flame nozzle was 10 mm, and the test time was 20 s. After exposed to the violent oxyacetylene flame, the ablative rates, including the erosion rate (R_L) and the mass loss rate (R_m), were calculated according to the following equation.

$$R_L = \frac{L - L_a}{t} \quad (2)$$

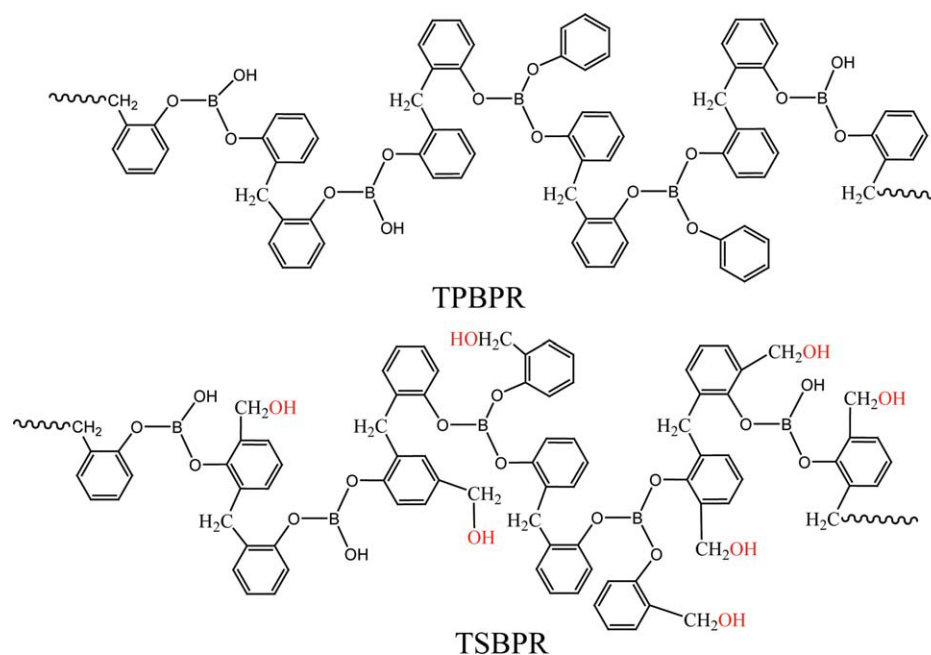
$$R_m = \frac{m - m_a}{t} \quad (3)$$

where, L and m were the thickness and mass of the ablative sample before ablated, respectively. L_a and m_a were the thickness and mass of the insulation sample after ablated, respectively. In addition, t was the ablation time, which was 20 s in this work.

RESULTS AND DISCUSSION

Structure of TPBPR and TSBPR

The chemical structure and FTIR spectrums of TPBPR and TSBPR were shown in Scheme 1 and Figure 1, respectively. It can be seen that there are a lot of methylol groups (–CH₂–OH) in TSBPR but not in TPBPR, which had been confirmed by Zhang.⁹ What is more, both the resins also present the same absorption bands except a methylol group absorption band at 1017 cm⁻¹. In addition, the slight absorption bands at 1381 cm⁻¹ implies there are some B–O linkage from the reaction of boric acid and phenol in the two kinds of resins.¹⁸ Moreover, the absorption bands at 756 cm⁻¹ are much stronger than that at 826 cm⁻¹, which indicates that the reactions between phenol borate and formaldehyde mainly happen at the ortho position of the benzene ring when the resins are synthesized.¹⁹ Generally, the molar ratio of phenol and formaldehyde was



Scheme 1 Molecular structure of TPBPR and TSBPR. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

controlled severely more than 1.0 when the TPBPR was synthesized. As a result, the methylol groups generated are reacted by redundant phenol completely. However, when the TSBPR was synthesized, the molar ratio was less than 1.0. Thus, the redundant formaldehyde will further react mainly at the ortho position of the benzene ring to form some active methylol groups.⁹ Finally, the absorption band of methylol group at 1017 cm^{-1} is observed only in the TSBPR, which implies that the TSBPR will be cured further once it is heated to a higher temperature.²⁰

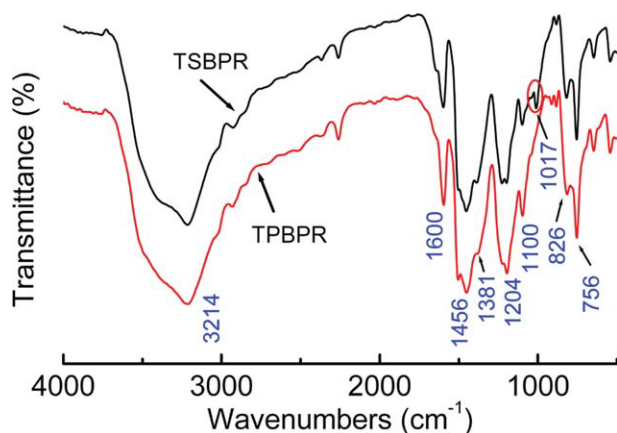


Figure 1 FTIR of TPBPR and TSBPR. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TG and DSC of TPBPR and TSBPR

The TG, DTG, and DSC curves of two kinds of resins were measured and shown in Figure 2(a–c), respectively. It can be seen that both the resins present the similar TG and DTG results under the protection of nitrogen. However, the carbon residue of TPBPR is slightly lower than that of TSBPR, although the degradation temperature of the former (154.9°C) is gently higher than that of the latter (149.5°C) at 800°C . That means the thermal stability of TPBPR is gently higher than that of TSBPR mainly due to the molecular weight of the former is much higher than that of the latter. However, some six-membered ring structures containing $\text{B} \leftarrow \text{O}$ coordination bond are formed in TSBPR (not in TPBPR) after TSBPR is cured at high temperature to improve the carbon residue of TSBPR.^{18,21} Furthermore, Figure 2(c) shows that there are two endothermic peaks and one strong exothermic peak in the DSC curves of TSPBR. The first endothermic peak confirms TSBPR will be melted at 139.5°C . The second endothermic peak at 161.9°C may be attributed to its quick thermal degradation.⁹ Moreover, the strong exothermic peak at 155.5°C indicates that TSPBR will be cured further because there are some active methylol groups in TSBPR molecular structure. However, TPBPR is hardly melted until the temperature is over 171.8°C mainly due to its much higher molecular weight than TSBPR. Obviously, the melting temperature of TSBPT is not only lower than that of TPBPR but also lower than the vulcanization

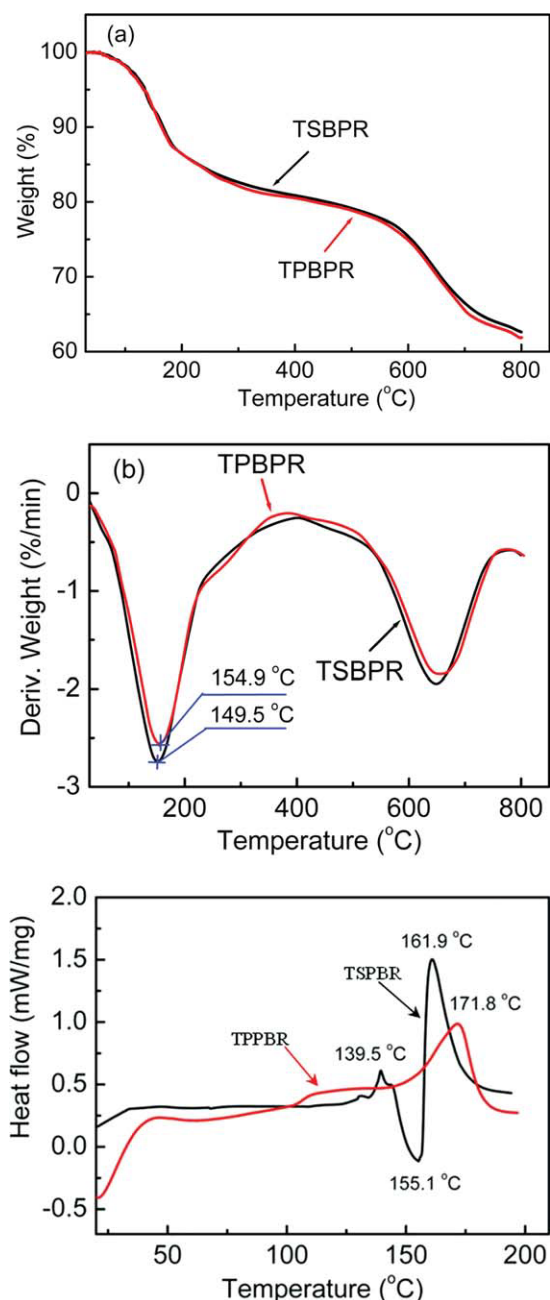


Figure 2 (a) TG, (b) DTG, and (c) DSC curves of TPBPR and TSBPR under nitrogen at a heating rate of 20°C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

temperature (160°C in this research). Therefore, TSBPR can be dispersed homogeneously in the EPDM matrix when vulcanized at 160°C.

Vulcanization behavior of the composites

Usually, the vulcanization time (t_{90}) of the rubber-based composites must be measured to evaluate their vulcanization behavior before they are vulcanized. Some studies had indicated that the vulcanization behavior of those composites was affected

TABLE II
Influence of TPBPR and TSBPR Weight Ratio on the Vulcanization Behavior of the Composites

Samples	t_{90} (min)	ML (Nm)	MH (Nm)
C0/20	31.67	0.097	1.026
C5/15	30.66	0.095	0.879
C10/10	29.28	0.094	0.794
C15/5	27.00	0.092	0.652
C20/0	22.62	0.091	0.501

greatly when TSBPR was introduced.^{9,10} Therefore, in this study, the effects of TPBPR and TSBPR weight ratio on the vulcanization behavior of the EPDM-based composites are shown in Table II. Apparently, the t_{90} of the composites decreases gradually with TPBPR content increasing and TSBPR content decreasing. In other words, TSBPR will prolong the vulcanization time of the composites heavily but TPBPR will not, presumably due to the methylol group of TSBPR weakening the vulcanization ability of the dicumyl peroxide. Furthermore, the torques at the vulcanization initial stage (ML) and at the maximum values (MH) of the composites are both decreasing continuously with the TPBPR and TSBPR weight ratio increasing, which implies that the weight ratio apparently affects the crosslink density of the composites.

As shown in Figure 3, the crosslink density of the composites decreases gradually via increasing TPBPR and TSBPR weight ratio. That confirms strongly that the lower molecular weight thermosetting boron phenolic resin will enhance the crosslink network severely for its curing reaction during the composites being vulcanized.

Effect of TPBPR and TSBPR weight ratio on mechanical properties of the composites

During the rocket motor charging, transporting, curing, and flying, the insulation composites have to

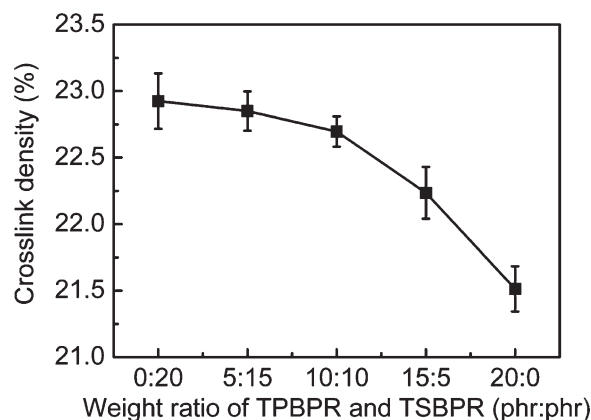


Figure 3 Effect of TSBPR and TPBPR weight ratio on crosslink density of the composites.

undergo a huge dimension deformation. Therefore, it is very necessary for these thermal insulation composites with strong tensile strength and big elongation to match the advanced rocket motor.¹⁷ As shown in Figure 4, with TPBPR and TSBPR weight ratio increasing, the strain range of the composites becomes wider and wider but their yield strength becomes smaller and smaller. As well known, the TSBPR has some active methylol groups in its molecule structure. It will be cured together with the EPDM matrix to enlarge the crosslink density of the composites during the composites being vulcanized at 160°C.¹¹ Consequently, the segment movement of the final TSBPR/EPDM product is restricted greatly. However, to TPBPR, there are not any active methylol groups in its molecule structure. It will not react with EPDM rubber and still keeps its linear molecule structure during the vulcanization of the composites. The yield strength of the composites gradually decreases with TPBPR and TSBPR weight ratio increasing.

In addition, the effects of TPBPR and TSBPR weight ratio on the tensile strength and the elongation of the composites are shown in Figure 5. Obviously, besides the yield strength, the tensile strength of the composites decreases sharply until the weight ratio is 10 : 10, and then decreases slightly once it is over 10 : 10. Moreover, the elongation at break of the composites increases quickly via increasing the weight ratio of TPBPR and TSBPR. As a result, though the elongation of the composites added 20 phr TSBPR could not meet the need of the rocket motor, interestingly, it has been improved heavily when we add some TPBPR as the substitute of TSBPR in an equivalent dosage into the EPDM composites. For example, the elongation of the sample C10/10 exceeds 300% even when the content of

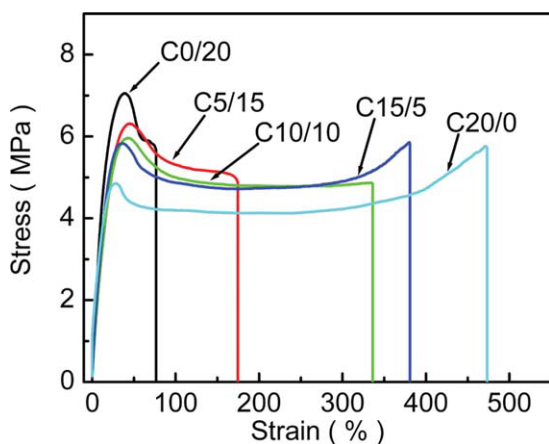


Figure 4 Effect of TPBPR and TSBPR weight ratio on stress–strain curves of composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

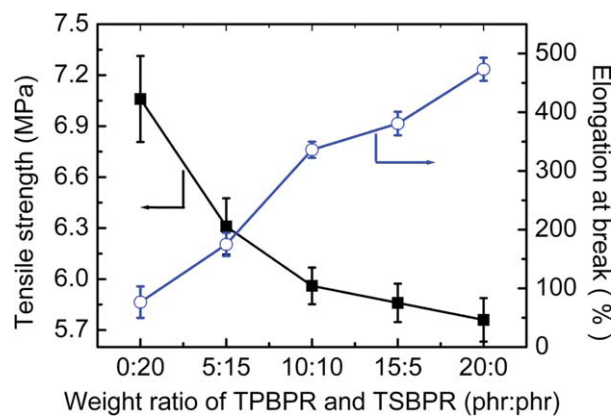


Figure 5 Effect of TPBPR and TSBPR weight ratio on tensile strength and elongation of the composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TPBPR is 10 phr, which is big enough to meet the need of the advanced rocket motor.

As discussed in section TG and DSC of TPBPR and TSBPR, the melting temperature of TSBPR is very low and it could be dispersed in the EPDM matrix more easily than TPBPR, which may make the interface bond strength between the short aramid fibers and the rubber matrix improved on the one hand. On the other hand, the polymerization of those thermosetting boron phenolic resins with the rubber improves the crosslink network of the composites under a high temperature condition.¹¹ As a result, the modulus and the tensile strength of the composites are improved together but the elongation of the composites is very small for the movement of polymer molecule chains is inhibited strongly. However, the glass transition temperature of TPBPR is higher than that of TSBPR. After blended with EPDM matrix and others additives, the resin still keeps grainy structure in the composites. The crosslink network of the composites could hardly be enhanced very much because there are not any active methylol groups in TPBPR. Therefore, the elongation of the composites becomes higher and higher with TPBPR and TSBPR weight ratio increasing.

The fracture morphology of the final composites also confirms the above conclusion. Therefore, the SEM pictures of three typical samples, C0/20, C10/10, and C20/0, are shown in Figure 6 to observe the dispersion of TPBPR and TSBPR in the vulcanizations, respectively. Obviously, sample C0/20 presents the best dispersion of TSBPR and sample C20/0 shows the poorest dispersion of TPBPR in the rubber mixture. As a result, a lot of big TPBPR particles agglomerated are observed in the TPBPR/EPDM composites. Dramatically, when TSBPR and TPBPR are blended and then added together into

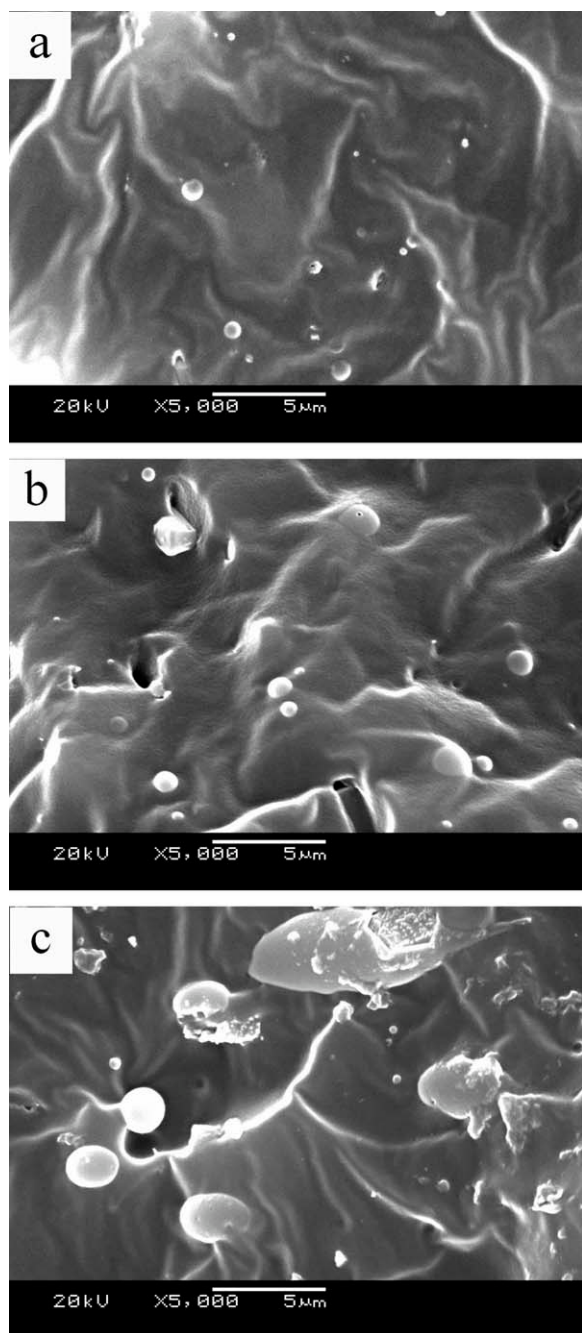


Figure 6 SEM picture of sample (a) C0/20, (b) C10/10, and (c) C20/0.

the EPDM matrix, the agglomeration of TPBPR is weakened greatly and their dispersions become very better in the final composites. As a result, the reinforcement of those resins on the composites is strengthened gradually with the increasing of TSBPR and the decreasing of TPBPR.

Aging behavior

Previous studies indicate that after the composites were stored more than 1 year, their elongation will

become smaller and smaller even when the original elongation is big enough.²² To explore the reasons, in this research, three typical vulcanized samples, sample C0/20, sample C10/10, and sample C20/0 were placed in an oven at 120°C for 0–14 h to compare their crosslink density changes. As shown in Figure 7, if only 20 phr TSBPR is added into EPDM composites, the crosslink densities of the composites increase quickly with the aging time protracting. This confirms that the TSBPR is cured incompletely when it is vulcanized with EPDM matrix at 160°C. Therefore, it will further polymerize slowly in the final vulcanization during the long-term storage even at room temperature. As a result, the elongation of the final composites becomes smaller and smaller with the store time protracting. However, for the sample C20/0, the crosslink density hardly changes via increasing the aging time, which means that the TPBPR cannot polymerize further to reduce the elongation of the final composites. In addition, the crosslink density of sample C10/10 increases slightly with the aging time increasing from 0 phr to 14 phr because 10 phr TSBPR has been substituted with 10 phr TPBPR. Therefore, TPBPR is the idea filler to improve the elongation of the thermal insulation composites.

Effect of TPBPR and TSBPR weight ratio on bond strength of the composites

In fact, all the thermal insulation composites must be adhered to the metallic wall of the rocket motor firmly to keep the motor flying safely. Usually, the chemlock-205 and chemlock-238 are both used to adhere to the composites to the metallic wall. However, in this study, the main aim is to evaluate the bonding properties of the composites reinforced by TPBPR and TSBPR only via changing the weight ratio of two kinds of resins. Therefore, only the chemlock-205 is used here as the adhesive between the

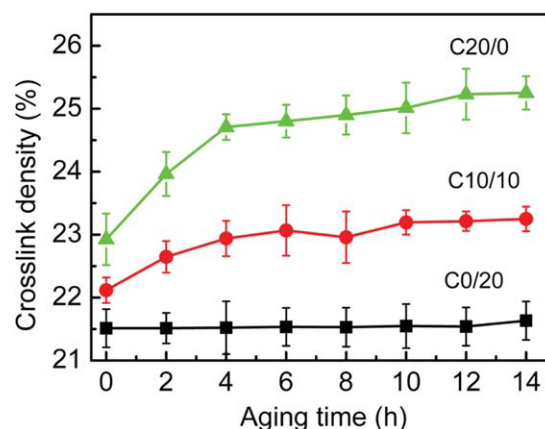


Figure 7 Effect of aging time on crosslink density of C20/0, C10/10, and C0/20. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

composites and 1045 (a carbon steel which contains about 0.45% carbon by weight according to ASTM standard). As shown in Figure 8, after chemlock-205 and the composites were vulcanized together between the double 1045 joints, the bond strength of the composites to 1045 presents a continuously decreasing tendency as the weight ratio of TPBPR and TSBPR increasing. In other words, the TSBPR can improve the bonding properties of the composites more heavily than TPBPR. The reason may be that the TSBPR could disperse easily in the EPDM rubber to improve the adhesiveness of the composite to the 1045. However, the molecular weight of TPBPR is much higher than that of TSBPR. It is very difficult for TPBPR to dissolve in the rubber matrix. As a result the TPBPR still keeps fine powder in the vulcanization. The adhesiveness of the final composites to 1045 joints becomes poorer and poorer, and the bond strength of the composites reduces gradually with the weight ratio of TPBPR and TSBPR increasing.

Effect of TPBPR and TSBPR weight ratio on ablative properties of the composites

Besides the big elongation, strong tensile strength, and strong bond strength, the ablative property is another important parameter to evaluate the thermal insulation composites because they have to endure the violent erosion and ablation of the combustion gas during the motor flying. Namely, the ablative rates of the composites should be as low as possible.²³ As shown in Figure 9, the ablative rates of the composites, including erosion rate and mass loss rate, are both increasing continuously with the weight ratio of TPBPR and TSBPR increasing. As discussed above, the TSBPR could be dispersed in the EPDM matrix easily but the TPBPR could not for its bigger molecular weight and higher glass transition temperature than TSBPR on the one hand. On

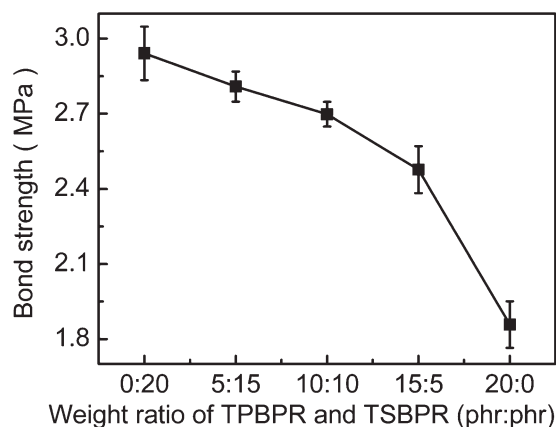


Figure 8 Effect of weight ratio of TPBPR and TSBPR on bond strength of the composites.

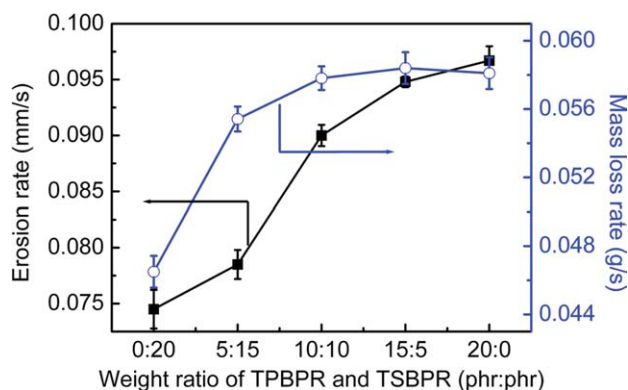


Figure 9 Effect of TPBPR and TSBPR weight ratio on ablative rates of the composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the other hand, the further polymerization reactions of TSBPR in the rubber mixture enhance the total crosslink network of the final composites heavily during the vulcanization process because TSBPR contains a lot of active methylol groups.^{11,20} As a result, the thermal stability and the fire resistant ability of the TSBPR are also higher than that of TPBPR, which is the main factor to improve the ablation resistant properties of the thermal insulation composites.

CONCLUSIONS

The mechanical, bonding, and ablative properties of the thermal insulation composites were investigated via changing the weight ratio of TSBPR and TPBPR resin in the short aramid fiber reinforced EPDM composites. The results indicate that with the weight ratio of TPBPR and TSBPR increasing, the elongation of the composites increases sharply as their crosslink density, tensile strength, and bond strength decrease gradually because the TPBPR does not polymerize further like the TSBPR during the vulcanization process. What is more, the ablation resistant properties of the composites also decrease continuously with the weight ratio of TPBPR and TSBPR increasing. Therefore, to obtain the very thermal insulation composite with the excellent comprehensive properties, the optimal weight ratio of TPBPR and TSBPR should be 10 : 10.

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