Effect of Magnesium Methacrylate and Zinc Methacrylate on Bond Properties of Thermal Insulation Material Based on NBR/EPDM Blends

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ABSTRACT: To improve the bond property between thermal insulation composites and metal surface, magnesium methacrylate (MDMA) and zinc methacrylate (ZDMA) were added into NBR/EPDM blends, respectively. The results indicated that the dispersion of MDMA powder was very well and its content changes much smaller in the composites than that of ZDMA. As a result, with the dosage of MDMA increasing from 0 phr to 7 phr, the polarity of MDMA/composites was improved gradually due to the increasing of ionic crosslink density and the decreasing of contact angle. Therefore, the bond strength of the composites to metal increased continuously. And the failures of bonding samples were all in MDMA/composites. After adding ZDMA instead of MDMA into the rubber, however, ZDMA powder would agglomerate during being vulcanized. Therefore, the bond strength of the composites firstly increased slightly and then decreased sharply once ZDMA was over 2 phr, whereas the contact angle of ZDMA/composites is much lower than that of MDMA/vulcanizates. Moreover, all the bonding samples failed at the interface of metal. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3901–3909, 2009

Key words: composites; strength; adhesives

INTRODUCTION

As an important component between the solid propellant and the metal wall in a solid rocket motor, thermal insulation materials are usually utilized to protect the integrality of the metal wall during the motor working. Recently, aramid fiber reinforced ethylene–propylene–diene terpolymer (EPDM) and EPDM-based thermal insulation materials have become the research focus in this field for their high thermal stability and strong ablation resistance ability.[1–6] However, these materials have to be adhered to the metal wall firmly to ensure the stability of rocket motor during flying. Unfortunately, the adhesive ability of the EPDM composite materials to the metal wall is very poor due to the huge polarity difference between the two kinds of materials. Thus, adhesives, such as chemlok (Load chemical Co., America), isocyanate, or megum-14135 (Rohmhaas Co.), were employed to improve their bond properties.[7–11] However, the introduction of adhesives causes new troubles. For example, the bubbles on the bond surface caused by the leftover of the solvent in these adhesives would reduce the adhesive strength significantly.[12] In addition, the vaporization of the solvent not only wastes a lot of time but also pollutes the environment of workshop.[13]

Another effective way to improve the bond strength between the composites and the metallic surface is introducing some polar organic fillers into EPDM matrix to reduce the polarity difference between them instead of using adhesives. β-unsaturated carboxylates are good choices because they contain ionic bonds and unsaturated double bonds. For peroxide-cured rubber system, polymerization, including homopolymerization and graft copolymerization, would happen in those unsaturated carboxylates initiated by peroxide during the vulcanization of rubber mixture. As a result, the mechanical and bond properties of the vulcanizates are improved because the composites polarity is enhanced by the introduction of polar groups.[14] For examples, it has been reported by Shanghai Jiaotong University that a series of metal salts of unsaturated carboxylates have been introduced into the rubber matrix.[15–18] The results showed that only zinc methacrylate (ZDMA) and magnesium methacrylate (MDMA) were able to improve the mechanical properties of vulcanizates significantly. Richard Costin added zinc

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TABLE I
The Formula of the Insulation Materials

Components	Part by weight (phr[a])
EPDM	70
NBR	30
DCP	4
Chloroparaffin	10
Antimony trioxide	5
Boron phenolic resin	20
Fumed Silica	20
Aramid fiber	15
MDMA (or ZDMA)	0–7

[a] phr is the parts by weight per 100 parts by weight of rubber

acrylate (ZDA) into acrylonitrile–butadiene rubber (NBR) to improve the bond properties of the rubber to metals.[19] The bond strength could reach 3.4 MPa when 2 phr ZDA is added without any adhesives. Liu et al. added ZDA into EPDM rubber to improve the bond properties of vulcanizates to metal as well.[20] Unfortunately, the bond strength was only 1.8 MPa after 3–6 phr ZDA is added in the EPDM. In addition, Wang introduced MDMA into NBR and obtained the very composites with high bond strength.[21] However, to the author's knowledge, the introduction of MDMA into EPDM rubber, especially the thermal insulation composites based on EPDM, has not been reported so far.

To improve the bond property between the insulation material based on EPDM and metal (such as 1045, a carbon steel that contains about 0.45% carbon by weight according to ASTM standard) without adhesives, in this research, MDMA powder and NBR were added into EPDM matrix system. ZDMA powder and NBR introduced into EPDM mixture with the same dosage and process were studied for comparison. The results show that the bond strength of MDMA/composites to 1045 is much higher than that of ZDMA/composites to 1045.

EXPERIMENTAL PART

Materials and specimen preparation

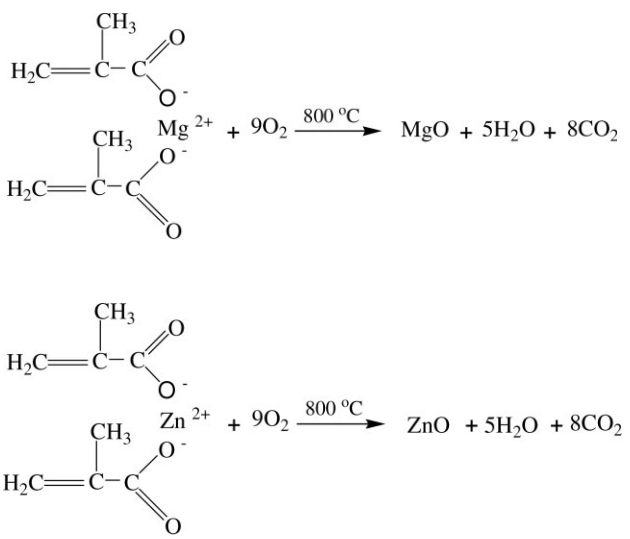
MDMA powder or ZDMA powder with a particle size of 100 mesh supplied by Xi'an Organic Chemical Industry Plant (China) was added into rubber blends of EPDM (EPDM4045, Jilin Chemical Co., China) and NBR (NBR26, Lanzhou Petrochemical Co. Ltd., China). The rubber mixtures were prepared by blending aramid fibers (Twaron1001, Akzo Co. Ltd, Holland) with 12 μm in diameter and 5 mm in length, fumed silica (A-200, Jilin Shuanglong Chemical Co. Ltd., China) and boron phenolic resin (FB, Xi'an Taihang Fire Retardant Co., China) in a two-roll mill. Then the flame retardants (chloroparaffin, Shanghai Jieren Chemical Co., China and antimony trioxide, Huachang Antimony Industry Co. Ltd, China) and the vulcanization agent (dicumyl peroxide, DCP, Shanghai Fangruida Co. Ltd, China) were also added into the rubber mixtures, respectively. The detailed formula was listed in Table I.

After MDMA (or ZDMA), short fibers and the other additives were well dispersed in the NBR/EPDM rubber in the two-roll mill for about 20 min, the mixture were rolled into thin sheet with a thickness of 4.0 mm along the direction of machine rolling. Then the thin sheet was placed between two 1045 plates and put into a mold for vulcanization at 160°C and 15 MPa for 50 min. The plates with a diameter of 25.0 mm had been pretreated with Al_2O_3 (120 mesh) abrasive cloth and cleaned with acetone before used.

Properties test

Purity of ZDMA and MDMA powder

The purities of ZDMA and MDMA were measured via burning their powder in a Muffle Furance at 800°C for about 6 h until the residue weight presented a constant. Because the powder had been extracted by acetone and dried in a vacuum oven before added into the rubber compounds, only some residual ZnO or MgO may exist in the ZDMA or MDMA powder. Therefore, the main reactions during the powder burning were shown as following:



Obviously, only some metal oxides, such as ZnO and MgO were left in the residue after the powders burned thoroughly. Consequently, the purity of the powder can be calculated according to the following equation through weighing the powder and its residue.

$$\text{Purity } (\%) = \frac{M(a-b)}{154a} \times 100 \qquad (1)$$

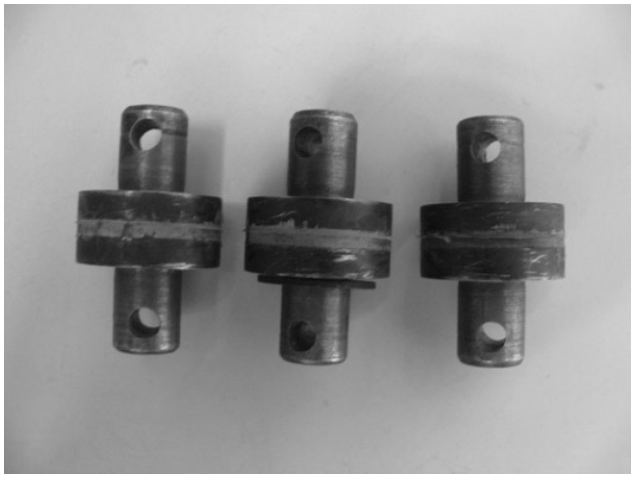


Figure 1 The bonding samples after vulcanization (without using any adhesive).

where M is the molecular weight of ZDMA (235) or MDMA (194), a is the mass of ZDMA or MDMA powder, b is the mass of ZnO or MgO residue, respectively.

Bond strength and fracture morphology

The vulcanized bonding samples as shown in Figure 1 were tested on a CMT4104 tensile electron machine following the procedure described in ASTM D2919-01. And the crosshead speed was 50 mm/min. Then the bond strength (σ) was calculated according to the following equation:

$$\sigma = \frac{F}{A} = \frac{4F}{\pi d^2} \tag{2}$$

where F is the tensile strength, A *is* the area of bonding surface of 1045 plates, and d is the diameter of 1045 plates, in this research, 25.0 mm.

After disjoined, the fracture morphology of the bonding samples was pictured with a digital camera (SONY α700) to analyze the failure modes of the bonding samples. In addition, the longitudinal profile of the vulcanizates was observed on a scanning electronic microscope (SEM, JSM-6460LV) to analyze the microstructure and distribution of MDMA or ZDMA powder in the composites. An energy dispersive spectrometer (INCAEnergy, Oxford instrument company, England) equipped in this SEM could also examine the changes of Mg or Zn content in the composites with a line scan to the materials' longitudinal profile.

Contact angle of the insulation material

To evaluate the polarity of the insulation materials reinforced by MDMA or ZDMA with different dosages, the contact angle of vulcanized composites was carried out on a contact angle meter (OCA20, Dataphysics Company, Germany) through a droplet of distilled water on the surface of vulcanizated composite materials.

Crosslinking density of the insulation material

The crosslinking density was determined by the equilibrium swelling. After vulcanization, 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 size does not change anymore. The weight of the samples was measured after fully swollen. Then the samples were completely dried under reduced pressure 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:

$$V_{\mathrm{r}} = \frac{m_0\varphi(1-\alpha)\rho_r^{-1}}{m_0\phi(1-\alpha)\rho_r^{-1} + (m_1 - m_2)\rho_s^{-1}} \tag{3}$$

where m_0 is the sample mass before swollen, m_1 and m_2 are the swelled sample masses before and after dried, respectively, φ is the mass fraction of NBR/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. To distinguish ionic crosslinking from covalent crosslinking, the above samples were swollen in a mixture of toluene and chloroacetic acid once again for 120 h to destroy ionic crosslinking, followed by swelling in toluene for 72 h and weighed, then vacuum dried and reweighed. V_{r1} was calculated from eq. (2), which represents the covalent crosslinking density. V_{r2}, which is calculated by subtracting V_{r1} from V_r, was used to represent the ionic crosslinking density.

RESULTS AND DISCUSSION

Purity of ZDMA and MDMA

It is well known that only the pure unsaturated carboxylate in the powders is effective to improve the bond strength between the insulation materials and 1045. However, some unreacted metal oxide, such as ZnO or MgO, may exist in the unsaturated carboxylate powders although the unreacted methacrylic acid had been extracted by acetone before added into the matrix compounds. Therefore, the purities of those powders used are measured using thermal analysis as discussed in Experimental Part section and shown in Table II. The results indicate that the purities of ZDMA and MDMA in their powder are above 98.5%, which means the impurity in the powder is so little that it hardly affects the bond property of the composites to 1045.

TABLE II
Purities of ZDMA and MDMA Powder

Materials	ZDMA powder	MDMA powder
a (g)	10.1317	6.2011
b (g)	3.5512	1.3352
Purity (%)	99.11	98.85

Bond strength of the insulation materials

Figure 2 is SEM picture of one 1045 plate after polished with Al_2O_3 (120 mesh) abrasive cloth and cleaned with acetone. A lot of amorphous grooves at the surface of plate are observed, which are necessary to anchor the insulation material firmly during vulcanization. Figure 3 shows the effects of the dosage of ZDMA or MDMA in the range of 0–7 phr on the bond strength of thermal insulation materials. The bond strength of vulcanizates without ZDMA and MDMA has reached 2.65 MPa due to the introduction of 30 phr NBR in the 70 phr EPDM. But it still could not meet the requirement of rocket motor. The introduction of MDMA leads to a significant improvement in the bond strength of the vulcanizates to 1045. As shown in Figure 3, with the increasing of the MDMA dosage, the bond strength between 1045 and NBR/EPDM vulcanizates is increasing continuously and reaching maximum when 5.5 phr MDMA is added. This indicates that the introduction of MDMA in certain content could improve the bond properties of the NBR/EPDM-based insulation materials between metal and vulcanizates strongly. But too much MDMA particles would also cause the bond strength decrease of rubber composite. On the other hand, the introduction of ZDMA powder instead of MDMA leads to a completely different tendency in the bond strength of the insulation materials. With the increment of ZDMA dosage, the bond strength firstly increases and shows a maximum at 2 phr, then decreases sharply. The bond strength of the composites is even lower than that of the pure NBR/EPDM vulcanizates when more than 2 phr ZDMA is added. At the same dosage, the introduction of MDMA results in much higher composite bond strength than that of ZDMA. That means the reinforcement of ZDMA on the bond strength of rubber composite is much lower than that of MDMA. Therefore, the ideal filler is not ZDMA but MDMA to obtain the excellent bond properties between insulation materials and metal.

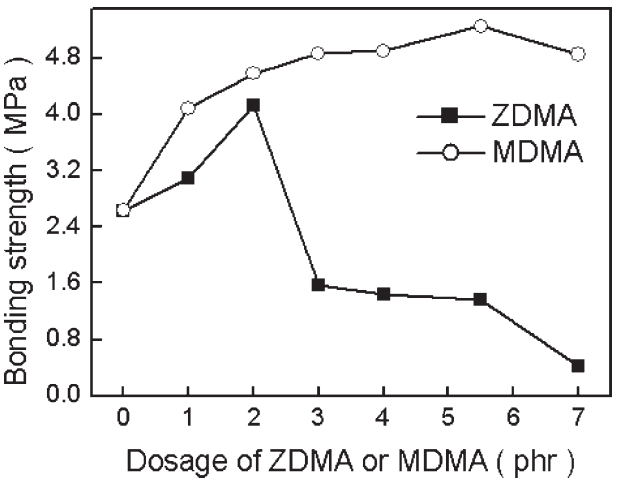


Figure 3 Effect of ZDMA and MDMA dosage on bond strength of insulation materials.

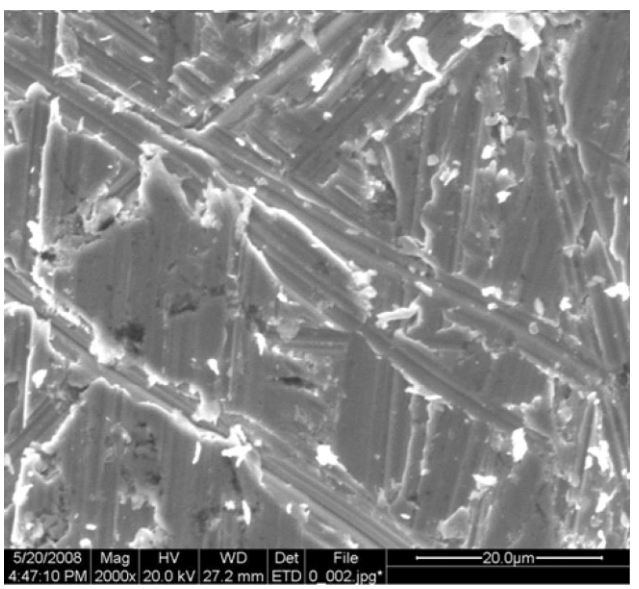


Figure 2 SEM picture of 1045 plate surface.

Crosslinking density and contact angle of insulation material

The main role of unsaturated carboxylates in the insulation material is to improve the affinity between composites and 1045 through enhancing the ionic crosslinking density and the polarity of the insulation materials.[7] As shown in Figure 4(a,b), the gross crosslinking density (V_r) and the ionic crosslink density (V_{r2}) are both increasing gradually with the dosage of ZDMA or MDMA increasing. Moreover, V_r and V_{r2} of the materials reinforced by MDMA are both higher than that of the materials reinforced by ZDMA although the dosage and the process of the materials are the same. It is well known that MDMA and ZDMA contain not only unsaturated double bond but also ionic bond. And the molecular weight of the MDMA is less than that of the ZDMA. Therefore, MDMA contains more ionic bond than ZDMA at the same weight. At high

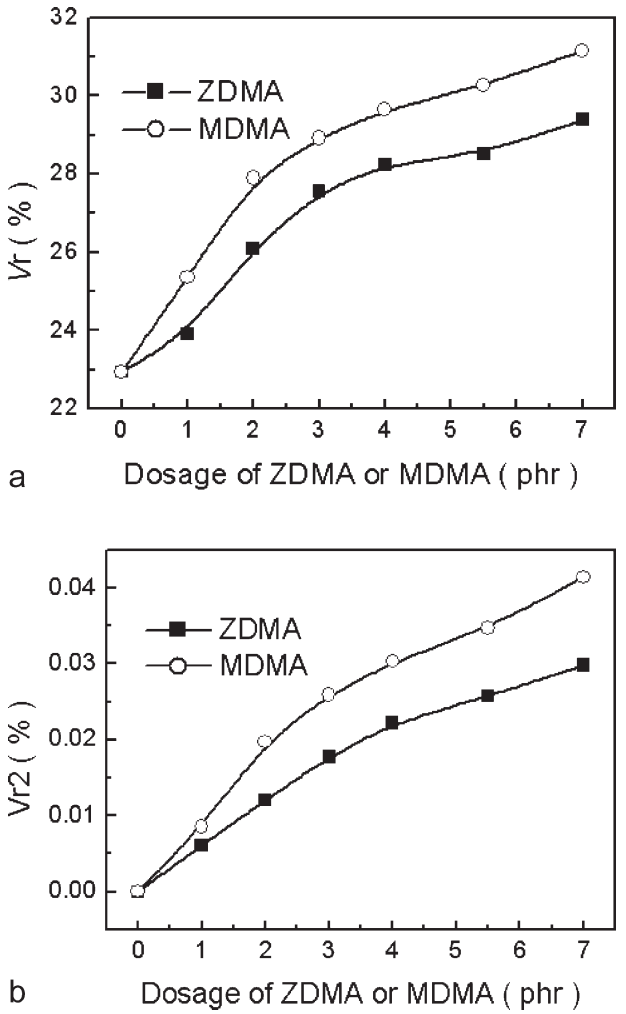


Figure 4 Effect of ZDMA and MDMA dosage on crosslink density of insulation materials [(a), gross crosslink density (V_r); (b) ionic crosslink density (V_{r2})].

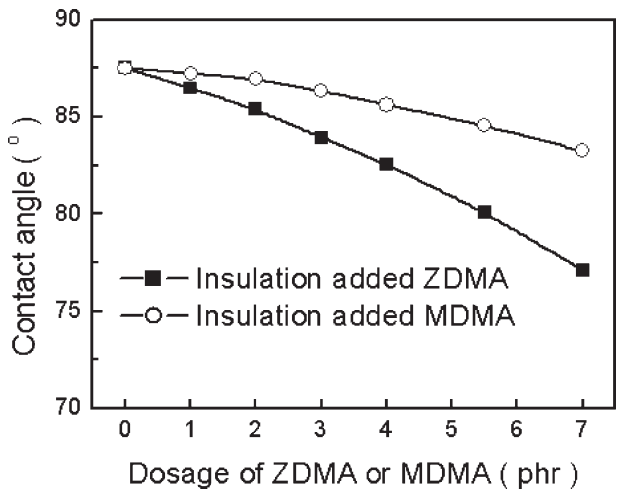


Figure 5 Effect of ZDMA and MDMA dosage on contact angle of insulation materials.

temperature, the free radical from the decomposition of peroxide could initiate the crosslinking of rubber and the polymerization of metallic methacrylate simultaneously, including the homopolymerization of metallic methacrylate and its graft-polymerization to the rubber matrix.[13,17] As a result, both the gross

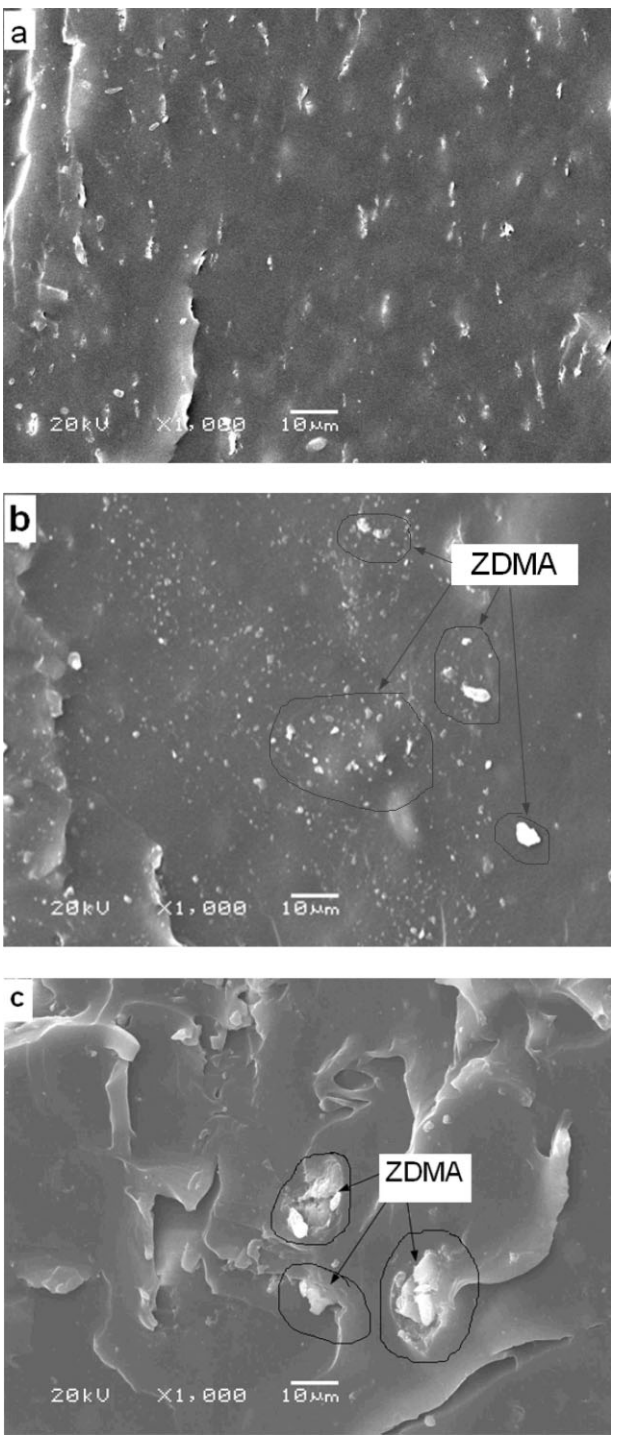


Figure 6 SEM pictures of vulcanized composites added 4 phr MDMA (a), 2 phr ZDMA (b), and 4 phr ZDMA (c), respectively.

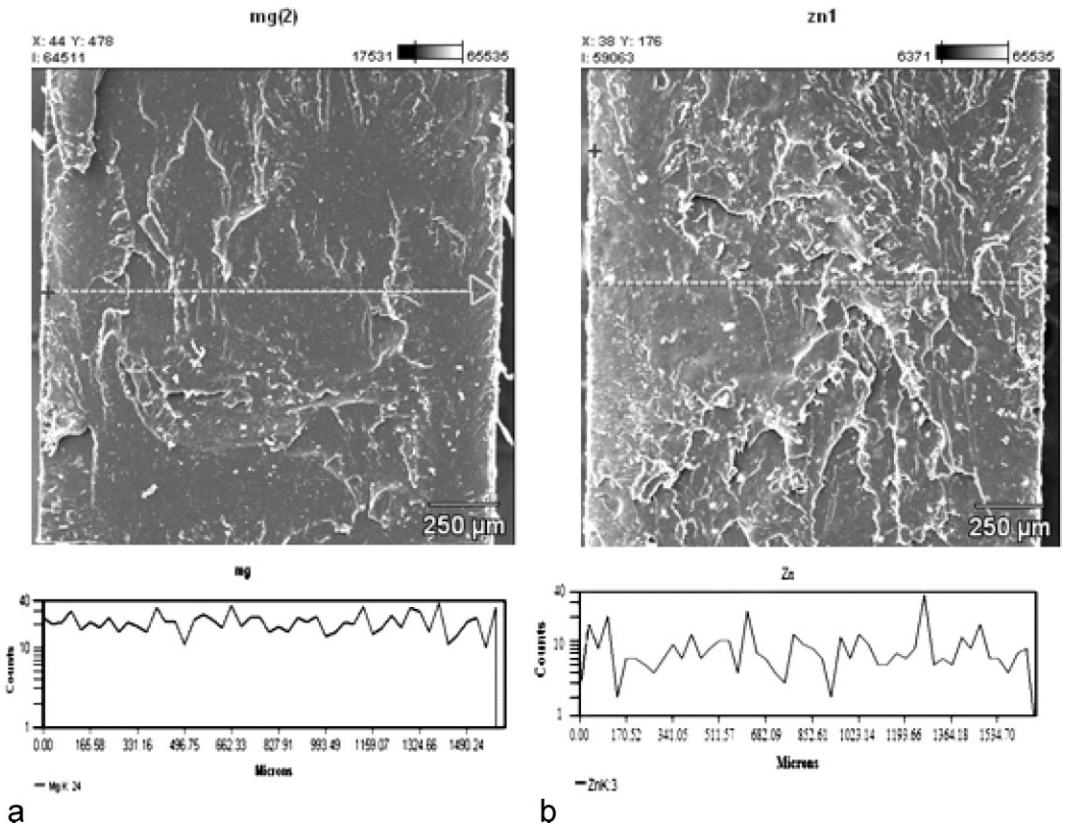


Figure 7 The distribution of Mg (a) or Zn (b) content in the longitudinal profile of vulcanized composites with a line scan.

crosslinking density and the ionic crosslinking density increase.

The effects of ZDMA and MDMA dosage on the contact angle of the insulation materials are shown in Figure 5. It has been well studied that the polarity of composite rubber or adhesive and its bond strength between the adhesives and the metallic substrate have positive correlation.[22,23] The polarity of composites is usually characterized by a contact angle of vulcanizates with a droplet of distilled water or other liquid.[24–26] As shown in Figure 5, the composite material still presents some polarity and its contact angle is less than 90°, although without ZDMA and MDMA thanks to the introduction of 30 phr NBR and some other polar additives. However, with the increment of ZDMA or MDMA, the contact angle of the composites with MDMA decreases slightly, whereas the contact angle of vulcanizates with ZDMA reduces sharply. In addition, the contact angles of the insulation materials with ZDMA are all much lower than that of the insulation materials with MDMA at the same dosage. This implies that the polarity of the ZDMA is much higher than that of MDMA and NBR/EPDM matrix.

As well known, the strong polar compound will aggregate in the nonpolar rubber matrix during vulcanization process. If the polarity difference is big enough between polar compound and rubber mixture, the compatibility between them would be reduced, which would cause a serious phase separation. As a result, the bond and mechanical properties between the phases are reduced. As discussed above in section Bond strength of the insulation materials, the bond strength firstly increases slightly until the dosage is 2 phr and then decreases sharply once the ZDMA dosage is over 2 phr. The reason is that the polarity of ZDMA is so high that the compatibility of ZDMA and NBR/EPDM mixture is very poor. Only when the content of ZDMA is very little (less than 2 phr) it can disperse very well in the mixture. But the agglomeration of ZDMA in the composites is strengthened sharply and impacts the bond strength finally once the dosage is over 2 phr. So the bond strength of composites filled with 2 phr ZDMA is gently higher than that filled with 1 phr MDMA although the former has much higher gross and ionic crosslinking density and lower contact angle. However, the polarity of MDMA is much lower than that of ZDMA and its compatibility with the rubber mixture is better than that of ZDMA. The agglomeration of MDMA in the mixture seldom happens during vulcanization unless the dosage of

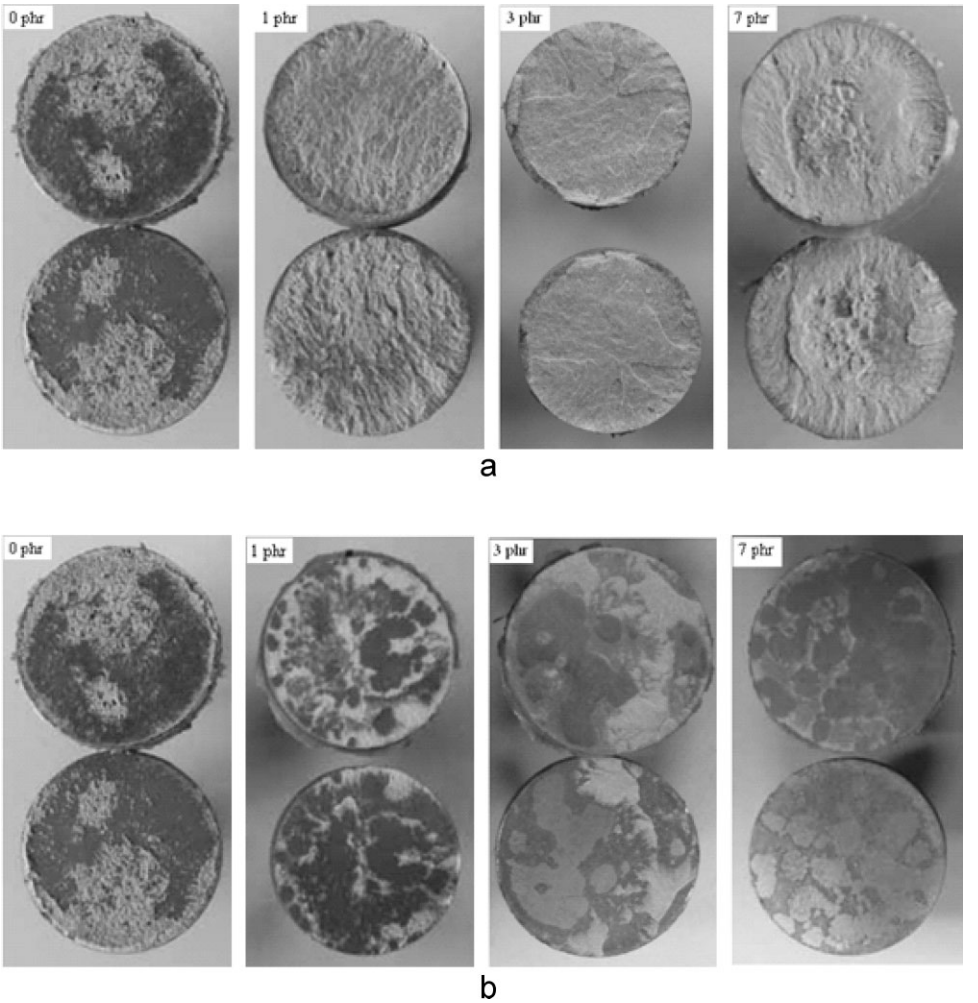


Figure 8 Fracture morphology of bonding samples after disjointed [(a) MDMA/composites; (b) ZDMA/composites).

MDMA is excessively high (such as 7 phr). As a result, the bond strength increases gradually with the increment of MDMA before 7 phr. Moreover, the slight decreasing in bond strength indicates the aggregation of MDMA powder in the composites may also happen once its dosage is over 5.5 phr for its higher polarity than the matrix. As a result, the dispersion of these powders is not very well and the bond property will be impaired.

Agglomeration of ZDMA powder

The longitudinal profile of the vulcanizates with 4 phr MDMA, 2 phr and 4 phr ZDMA were pictured with SEM as shown in Figure 6(a–c), respectively. It indicates that the distribution of MDMA powder is very well in the matrix and no aggregation of MDMA powder in the longitudinal profile of vulcanized composites is observed in Figure 6(a) after 4 phr MDMA is added. In addition, Figure 6(b) indicates that ZDMA powder can be well dispersed in the rubber mixture at a low dosage (2 phr). But its dispersion is even not better than that of 4 phr MDMA powder and the agglomeration occurs more or less in the longitudinal profile. However, the dispersion becomes very poor and the powder aggregates sharply as shown in Figure 6(c) when the dosage of ZDMA is 4 phr although the same process is followed to disperse the two kinds of powder in the composites. That means the poor bond property of ZDMA/composite may be caused by the aggregation of ZDMA powder in the composite due to its poor compatibility with rubber matrix.

Moreover, the changes of Mg and Zn content in the vulcanized composites also indicate that aggregation of ZDMA powder. As shown in Figure 7, the changes of Mg content [Fig. 7(a)] are much less than that of Zn content [Fig. 7(b)] in the whole longitudinal profile of the composites. It also presents that ZDMA powder has agglomerated in the composites

but MDMA not. Finally, the serious agglomeration of ZDMA in the composites lowers the bond strength between 1045 and materials added ZDMA.

Fracture morphology of the bonding samples

To analyze the failure modes of bonding samples, the fracture pictures of the dual 1045 plates after disjoined are shown in Figure 8(a,b), respectively. Obviously, without being added ZDMA or MDMA, there is a black oxide layer at the surface of metal and vulcanizates and the failure modes belong to the interfacial failure. As a result, the bond strength between metal and insulation materials is too small to meet the need of solid rocket, whereas 30 phr NBR has improved the polarity of the insulation. However, after added those unsaturated carboxylates into the rubber mixture, the interface oxidation has been weakened significantly, which is consistent with results reported in the Refs. [13–15]. The composites filled with MDMA are anchored firmly to the metal surface grooves because the ionic bond is introduced and the polarity is strengthened after adding MDMA into the composites. As a result, the interface failure of the bonding samples is changing to the rubber failure and the surfaces of two 1045 plates are both coated by vulcanizates firmly after disjoined. Therefore, the bond strength is improved gradually with the increasing of MDMA shown in Figure 3. The introduction of MDMA at a high dosage would also damage the strength of rubber composite, which leads to a lower bond strength of the composite to the metal.

As shown in Figure 8(b), after added 1–7 phr ZDMA solely, the vulcanizates also have stronger antioxidative capability. As a result, the interface oxidation of the metal is lowered continuously with ZDMA dosage increasing. In addition, the ZDMA powder is still dispersed well at a low dosage. Therefore, the bond strength of the insulation materials added 1–2 phr ZDMA is much higher than that of the vulcanizates without ZDMA. However, because the polarity of ZDMA is much bigger than that of rubber mixture, the compatibility between ZDMA powder and rubber matrix is much poorer than that between MDMA powder and matrix. Therefore, the strong polar ZDMA powder will agglomerate together in the composites to impair their bond property to the metallic substrate during being vulcanized by peroxide once the dosage is more than 2 phr. As a result, the area in one of the dual 1045 plates coated by the vulcanizates becomes less and less and the debonding area becomes bigger and bigger at the metal surface when the dosage of ZDMA changes from 3 to 7 phr. In addition, all the bonding samples fail at the surface of metallic substrate, which confirms that ZDMA is not the ideal filler to improve the bond properties of thermal insulation materials based on EPDM although it has enhanced the ionic crosslink density and the polarity of the insulation materials.

CONCLUSION

In this study, the bond properties of the thermal insulation materials based on EPDM have been investigated systematically via adding MDMA or ZDMA powder into the matrix. The results indicate that MDMA is the ideal filler to improve the bond strength of insulation materials although both of them present the excellent purity. With the increasing of MDMA dosage, the gross crosslinking density and the ionic crosslinking density are both increasing continuously, and the contact angle is decreasing gradually. All the bonding samples fail in the vulcanized composites during being disjoined and display higher and higher bond strength with the increasing of MDMA dosage. However, after adding ZDMA instead of MDMA into the matrix, the bond strength of the composites firstly increases slightly then decreases sharply once the dosage is over 2 phr, whereas the contact angle of ZDMA/composites is much lower than that of MDMA/composites. The failure in ZDMA/composites and the distribution of ZDMA in the composites testify that the agglomeration of ZDMA in the insulation materials are intensified during vulcanization because the polarity of ZDMA is much higher than that of MDMA and NBR/EPDM mixture.

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