A new ionic cross-linking network type high hysteresis oil resistant ACM/POM TPV preparation method and performance research

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Research Article

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A new ionic cross-linking network type high hysteresis oil resistant ACM/POM TPV preparation method and performance research

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Abstract
In the article, the concept of ionic cross-linking was introduced into the preparation of TPV for the first time, and the dynamic full vulcanization technique was adopted to prepare acrylate rubber (ACM)/polyoxymethylene formaldehyde (POM) thermoplastic vulcanizates using Ca(OH)_2 as cross-linking agent, and ACM/POM TPVs completely different from the traditional covalent bonding vulcanization system were obtained. The physical and mechanical properties, aging resistance, dynamic mechanical properties, micromorphology, and energy loss of the composites under covalent crosslinking networks and ion cross-inking networks with different degrees of crosslinking were systematically studied. The results showed that Ca^{2+} could form metal ion binding with the -COOH of ACM, attracting each other to form ion clusters and playing a crosslinking role for ACM. Compared with the traditional covalent bond system, the TPV under the ionic bond system can be increased by a maximum of 31%, and the elongation can be increased by 14.5% under the 100% shape variable.
After stretching, the system shows higher permanent deformation, a higher energy storage modulus, and a higher loss modulus in the range of 95~140 °C, showing higher hysteresis. With the increase in Ca(OH)$_2$ dosage, the crosslinking density of ACM increases gradually and decreases at 8 phr. The increase in dispersed phase modulus increases the phase domain of dispersed phase, weakens the binding with matrix, weakens the tensile strength, increases the intrusion of hot oxygen and hot oil, increases the energy storage modulus, and decreases the loss modulus.

**Introduction**

Thermoplastic vulcanizates (TPVs) are a kind of thermoplastic elastomer with the fastest growth in consumption in recent years.[1-4] TPVs products independently developed by many countries have been published successively, and more and more types of TPVs are gradually involved in multiple fields of production and life. TPVs consist of high-content crosslinked rubber as the dispersing phase and low-content thermoplastic as the continuous phase and are prepared by a special polymer reactive blending technique called dynamic vulcanization (DV).[5-7] Compared with traditional copolymerization and simple blending thermoplastic elastomers, TPVs have excellent mechanical properties, a lower compression set, fatigue resistance, dielectric resistance, repeatable machining performance, etc.[8-12] But TPVs often have difficulty maintaining good performance at high temperatures or in hot oils due to the presence of continuous plastic phases. Cui et al.[5] used methyl vinyl silicone rubber (MVQ) as the rubber phase and thermoplastic polyurethane (TPU) as the continuous phase, dynamically vulcanized a kind of high temperature-resistant TPVs, and studied the performance changes of TPVs under different vulcanization systems and dosages. They found that the TPVs with 1.5 phr 2, 5-dimethyl-2, 5-di (tert-butylperoxy) hexane (DBPH) as vulcanizing agent have the best heat-resistant oxygen aging performance, tensile strength, and better dispersion. Carboxyl acrylate rubber (ACM) is an elastomer obtained by copolymerization of acrylic ester as the main monomer. Its main chain is a saturated carbon chain, and the side groups are polar ester and carboxyl groups. This structural feature makes ACM have a wide range of
applications in the field of oil and high temperature resistant automotive parts, which can be used in automotive seals, O-rings, gaskets, and adhesives. In order to further improve the strength of materials and achieve the purpose of lighter weight, ACM has been gradually introduced into the research, preparation, and production of TPVs. Using ion-crosslinked ACM to prepare TPVs can further improve the stress resistance ability of composite materials under small deformation and improve the problem of insufficient fluidity in TPVs processing caused by large ACM content.\textsuperscript{[13,14]}

The research of crosslinking carboxyl rubber can be traced back to the 1950s.\textsuperscript{[15]} Brown\textsuperscript{[15,16]} obtained the "ion crosslinking" material by cations complexing the acid ions in it and carried out pioneering research based on the terpolymer of butadiene-acrylonitrile-acrylic acid made by Goodyear Company. In addition to carboxylate ionic ionomers, there are also sulfonic acid ionomers, sulfhydryl ionomers, and phosphoric acid ionomers.\textsuperscript{[17]} But at present, the research on carboxylic acid type ionomers is more extensive in the world,\textsuperscript{[18]} mainly methacrylic acid type and acrylic acid type. Due to different activation energies, different types and prices of metal oxides, metal hydroxides, or metal complexes will lead to different vulcanization characteristics of rubber and vulcanizing properties. H. Matsuda et al.\textsuperscript{[19]} studied the preparation method of ionic crosslinked rubber by neutralizing the carboxyl terminal liquid rubber with metal oxides and metal carbonate and found that the tensile strength of rubber in bivalent metal ions has a rule of \( \text{Ba}^{2+} \geq \text{Ca}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} \), but the processing property of \( \text{Ba}^{2+} \) crosslinked rubber is poor. And they found that the ion-crosslinked rubber has repeatable properties that conventional rubber does not. Liang Shao et al.\textsuperscript{[20]} synthesized a new type of ion crosslinking agent from bis[3-(triethoxysilyl)propyl] tetrasulfide and zinc methacrylate as raw materials, which was used for crosslinking unsaturated rubber with a reversible ion three-dimensional structure. So that crosslinked styrene butadiene rubber (SBR) with considerable toughness can be recovered by the solution method and resynthesized by simply adding zinc oxide as a crosslinking agent. Yan Gao et al.\textsuperscript{[21]} used sodium and zinc acetate to neutralize the ethylene-acrylic acid copolymer and studied the influence of metal ions on the mechanical properties of the
ionomer. The results showed that the mechanical properties of the sodium ionomer increased with the addition of sodium salt, while the mechanical properties of the aluminum ionomer decreased with the addition of aluminum salt.

In this article, a new heat-resistant oil ACM/POM TPVs was prepared by using Ca(OH)$_2$ as the crosslinking agent of rubber phase. The crosslinking effect of metal ions was confirmed by Fourier transform infrared spectroscopy. Compared with the traditional covalent bond vulcanization system, the effects of the amount of crosslinking agent on the mechanical properties, aging resistance and dynamic mechanical properties of ACM and TPVs were systematically studied. The morphology of dynamically vulcanized ACM/POM blends was studied by scanning electron microscopy (SEM), and the optimal amount of crosslinking agent was finally determined.

Fig. 1 Schematic diagram of preparation of the ACM/POM TPV composites
Experiment

Material

Ethylene-acrylate elastomer, ACM, (121X, Mooney viscosity: 60 ± 5) was supplied by Jiujiang Dewey Rubber Technology Co. Ltd(China). Polyformaldehyde(POM), (HOSTAFROM®S9364, density: 1.36g/cm³, melting temperature(IOS 11357-1/-3): 166℃, melt flow rate: 4cm³/10min), was supplied by Celanese Corporation(America). Thermoplastic polyurethane elastomer(TPU), (hardness: 90HA), was supplied by Wanhua Chemical Group Co. Ltd(China). Hexamethylenecarbamate diamine(HMDC), (purity: 70%), was supplied by Ningbo Aikem New Material Co. Ltd(China).

Preparation of ACM/POM TPVs

Preparation of ACM vulcanizate

According to the formula in Table 1, prepare the ACM mix on the mixer. Add stearic acid and white carbon after the raw ACM roll slowly, and gradually open the roll distance to 2mm. Cut the rubber and make the triangle wrap. Different amounts of Ca(OH)₂ compound were obtained.

ACM master rubber was added into a 2mm mold and vulcanized in a plate vulcanizing machine. The vulcanizing temperature was 180℃, the vulcanizing time was 13min, and the vulcanizing pressure was 10MPa. ACM vulcanizing rubber with different dosage of vulcanizing agent was prepared and named Ca4-Ca8. Comparison with a covalently bonded cross-linked ACM performed using a 1.2phr HMDC, named H1.2.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Ca4</th>
<th>Ca5</th>
<th>Ca6</th>
<th>Ca7</th>
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<td></td>
<td></td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CTP</td>
<td></td>
<td></td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
</tr>
</tbody>
</table>

Tab. 1 Master rubber formula of ACM (Units: phr)
Preparation of ACM/POM TPVs materials

In ACM/POM TPV, TPU is used to toughen POM, and the mass ratio of ACM/POM/TPU is 65/28/7. The torque rheometer was used to melt ACM compound and POM. The processing process was as follows: The temperature of the torque rheometer was set at 180℃ and the rotational speed was 60rpm. POM and TPU were added into it, melting and blending for 5min, ACM compound was added, and the ACM was shear broken while vulcanized, and dynamic vulcanized for 8min.

The TPV was put into a 2mm mold and formed on a molding machine at 180℃. The preheating time was 3min, the molding time was 5min, and the pressure holding pressure was 10MPa. Then the TPV was taken out after cold pressing at 10MPa for 5min and named as TCa4-TCa8. The TPV corresponding to H1.2 is named TH1.2. The preparation process is shown in Fig 1.

Testing methods

Curing characterization and Torque curves of dynamic vulcanization

The vulcanization characteristics of ACM at the processing temperature were studied by GOTECH M-3000A RPA, determined the char time and vulcanization time, roughly judged the variation trend of vulcanization degree. The test temperature was 180℃ and the total test time was 20min.

The materials were mixed by HAAKE torque rheometer, and the numerical value of the blend materials' torque changes with time was automatically recorded by computer. Origin graphing software was used to draw the torque-time curve of the blend materials.

Gel volume fraction \( (V_r) \)

The gel volume fraction \( (V_r) \) in the rubber was measured by swelling method to characterize the apparent crosslinking density of ACM. The good solvent used for swelling was ethyl acetate and the swelling time was 24h. The formula (1) for calculating \( V_r \) is as follows:
\[ V_r = \frac{1}{1 + \frac{M_2 - 1}{M_1}} \frac{\rho_r}{\rho_s} \]  

_Equation (1)_

\( V_r \) is the gel volume fraction of rubber, \( \rho_r \) is the density of rubber before swelling,  
\( \rho_s \) is the density of the solvent, here is 0.902 g/cm\(^3\), \( \delta \) is the mass fraction of raw rubber in the formula, \( M_1 \) is the mass of the sample before swelling, \( M_2 \) is the mass of the sample after swelling.

_Fourier transform infrared spectrum (FTIR)_

Fourier Transform Infrared spectroscopy (FTIR) test: The Bruker Tensor 27 infrared spectrometer (Germany) recorded FTIR spectra in the wavelength range 800-3600 cm\(^{-1}\) using attenuated total reflection (ATR) mode.

_Mechanical characterization_

According to GB/T 528-2008 standard, using the I-7000S electronic tension machine produced by Taiwan High-speed Railway Testing Instrument Co. Ltd. to test the dumbbell type 2 sample, the speed was 500mm/min, and the test temperature was room temperature. According to GB/T 531.1-2008 standard test, using Shao A hardness tester for hardness test.

_Cyclic stretching and relaxation behavior_

The stress-strain process of ACM (300% shape variable) and TPV (100% shape variable) under two tensile cycles was recorded, and the tensile and recovery rates were both 100mm/min. The area enclosed by the stress-strain curve was calculated to characterize the energy loss of the material in the tensile process (\( W \)), and the energy loss rate (REL) was calculated by equation (2).

\[ \text{REL} = \frac{W}{W_0} \times 100 \]  

_Equation (2)_

\( W \) is the energy lost in a tensile cycle of the sample, namely, the integral area enclosed by the stress-strain curve; \( W_0 \) is the total energy required during the stretching process, i.e. the total area under the stretching curve.

_Dynamic mechanical property_

The variation of the stored modulus (\( G' \)) and loss modulus (\( G'' \)) of ACM and TPV with temperature was tested by RPA2000 rubber processing analyzer produced
by Alpha Technology Co. LTD. The test method was shear strain temperature scan, strain frequency was 1.7Hz, rotation Angle was 0.5°, and the scanning temperature range was 65~185℃.

**Scanning electron microscope (SEM)**

ACM/POM TPV samples with different Ca(OH)$_2$ dosages were brittle with liquid nitrogen. These TPV composites are placed on an aluminum bracket with a double adhesive carbon strip and then sprayed with gold. The fracture morphology was observed by field emission scanning electron microscope (SEM) of JEOL JSM-6700F under 5.0 kV acceleration voltage.

**Results and discussion**

**Fourier transform infrared spectrum (FTIR)**

In order to determine the feasibility of Ca(OH)$_2$ curing carboxylic acid type ACM by releasing Ca$^{2+}$, it is necessary to test the crosslinking network before and after the crosslinking to ensure that the vulcanization system is carried out according to the mechanism of metal ion curing carboxylated rubber. The Fourier infrared spectra of ACM raw gum, mixed gum after adding filler and vulcanization system, and vulcanized gum after vulcanization were tested respectively. The crosslinking condition was determined by the change in reactivity -COOH on ACM before and after crosslinking, and the results are shown in Fig 2.

![Fig. 2 Fourier transform infrared spectrum (FTIR) of ACM](image)

(a) Crude rubber (b) Mixed rubber (c) Vulcanized rubber
The side group of carboxyl type ACM is composed of a large number of ester groups and carboxyl groups, which is manifested as the carbonyl stretching vibration peak at 1731 cm\(^{-1}\) in the FTIR curve. By calculating the integral area of this peak, it is found that the integral area of ACM raw rubber is the largest, which is 5.19. When Ca(OH)\(_2\) is added and vulcanized, the characteristic absorption peak area here is 3.54, indicating that the carboxyl group of the ACM side chain is consumed. At the same time, a characteristic absorption peak absent in (a) and (b) appears in curve (c) at 1577 cm\(^{-1}\). This peak is the stretching vibration peak of the carbonyl group in metal carboxylate, indicating the formation of the metal carboxylate group.\(^{[19]}\) In combination with previous studies on ion crosslinking of carboxyl rubber and ionomers, the process of Ca(OH)\(_2\) crosslinking ACM is shown in Fig 3. Ca(OH)\(_2\) exudes the metal ion Ca\(^{2+}\) at high temperature, attacks the hydrogen on the carboxyl group of the ACM side chain, and forms a metal ion combination with it. The bivalent Ca\(^{2+}\) connects to the main chain of the ACM at both ends to form multiple heavy ion pairs, thus achieving the purpose of crosslinking. Such multiple heavy ion pairs can form an attraction through coordination bonds and van der Waals forces. Multiple ion pairs are attracted together to form ion clusters, further increasing the crosslinking density.\(^{[22]}\)

**Processing performance and curing characteristics**
Crosslink density is an important parameter to be investigated in vulcanization rubber. On the one hand, the different crosslink density of the rubber phase will affect its own performance in TPV; on the other hand, the difference in crosslink density brings about the change of modulus of two phases in the dynamic vulcanization process, which in turn affects the phase distribution when the two phases are co-mingled and finally changes the performance of TPV.

To determine whether the amount of Ca(OH)$_2$ would have a large effect on the crosslink density and modulus of the ACM phase, a vulcanizer test was performed on ACM at 180 °C to roughly predict its modulus change during the dynamic vulcanization process. The gel volume fraction of ACM Vulcanized rubber was also determined by the equilibrium swelling method to characterize the apparent crosslink density of the ACM phase. Fig 4(a) shows that with the increase in Ca(OH)$_2$ usage, the scorch time and vulcanization speed of ACM were slightly accelerated, but the Process curing time ($T_{90}$) was basically maintained at about 13 min, so the processing method of dynamic vulcanization (8min) + static molding (5min) was chosen for the subsequent TPV preparation. It is more obvious that the increase in Ca(OH)$_2$ use increases the maximum torque of ACM, but this increase only lasts until Ca7, when the Ca(OH)$_2$ use continues to increase, causing a decrease in the maximum torque instead. The difference between the highest torque and the lowest torque $M_{H}-M_{L}$ reflects the change of the crosslinking degree from the side, and Fig 4(b) summarizes the change pattern of $M_{H}-M_{L}$ and $V_r$. When Ca(OH)$_2$ increased from 4 phr to 7 phr, the $M_{H}-M_{L}$ of ACM increased from 4.96 dN·m to 7.56 N·m, and $V_r$ increased from 10.6% to 12.37%, and when the dosage reached 8 phr, both showed a significant decrease, indicating that too much Ca(OH)$_2$ does lead to a decrease in ACM crosslink density. From the mechanism of ACM ion crosslinking, it can be seen that when too much hydrogen on the carboxyl group is replaced by metal ions, the carboxyl group is completely blocked and cannot play the role of linking the two molecular chains, so that the crosslinking density is reduced.
Fig. 4 The vulcanization characteristics of ACM

(a) Vulcanization curve (b) Torque difference and degree of crosslinking

Fig. 5 (a) ACM/POM TPV torque rheological curve and (b) torque value changes

The ACM/POM TPV composites were prepared by the dynamic method. Fig 5 shows the torque curves and the variation of the dynamic vulcanization torque peak and equilibrium torque of the composites in the torque rheometer at different Ca(OH)$_2$ dosages. In the figure, 0~5 min is the torque peak after POM is added and melted at high temperature; the second peak at 5~6 min is generated by ACM compound added and softened; and then ACM is vulcanized and the torque rises. At the same time, the effect of heat and shear makes the ACM broken, and the crosslinking and breaking reach balance at 7~8 min, and the torque curve appears to peak, then the breaking process dominates and the torque decreases slowly, and the torque balance is basically reached at 13 min. With the increase of Ca(OH)$_2$ dosage, on the one hand, the crosslinking speed of ACM increases, and the degree of crosslinking is higher at the same time, so the torque of ACM/POM blends in 5~8 min is increased; on the other hand, the faster the modulus of ACM phase increases, the easier it is to be broken under the action of shear force; that is, the equilibrium point of vulcanization and
breaking is reached more quickly, and the peak position of dynamic vulcanization is more forward. However, early crushing does not mean that smaller phase domains are formed. ACM with a lower degree of crosslinking, on the contrary, tends to form smaller nano-rubber particles, and a lower degree of crosslinking means that the difference in modulus between the two phases is smaller, which can form a thicker phase interface thickness and a tighter bond between the two phases. As the degree of vulcanization increases, ACM becomes more difficult to crush into smaller particles, while the bond between the two phases is weak and prone to interfacial sliding, which also leads to a lower equilibrium torque.

**Mechanical properties**

The mechanical properties of ACM vulcanizates cross-linked by ionic bonding and those cross-linked by covalent bonding showed completely different characteristics. For this reason, a covalent bonding system (HMDC 1.2 phr) specimen with a similar crosslinking density to Ca4~Ca8 was selected for comparison, as shown in Fig 6. It can be seen that the specimens with HMDC 1.2 phr have a low constant tensile stress at strains from 0% to 300%, and the modulus increases as the strain continues to increase, while the Ca(OH)2 system has a large constant tensile stress at small deformations, and the modulus decreases slightly after a strain of more than 200%. The difference between the modulus changes of the two systems is mainly due to the different ways of bearing stress in the two types of bonds. The covalent bond system resists stress through the entanglement between molecular chains under small deformation, and when the molecular chains are stretched and oriented, the molecular main chains and cross-linked bonds start to resist stress, and the modulus appears to increase due to the high bond energy and the strong ability to resist stress. In the ionic bonding system in which Ca^{2+} forms multiple ions, these ion pairs are attracted to each other to form ion clusters, thus interconnecting the molecular chains. This connection is effective in transferring stress, but once an ion pair in this ion cluster is separated, the attraction between the remaining ion pairs is also reduced, leading to the collapse of the physical network formed by the ion cluster and the
reduction of the modulus. Fig 7 shows the stress-strain curve of the ACM/POM TPV. It can be seen from the figure that the reduction of modulus under this large deformation is more obvious in TPV, and the stress is basically no longer elevated after the strain reaches 200%.

![Stress-strain curves of ACM vulcanized](image)

![Stress-strain curves of ACM/POM TPV](image)

**Fig. 6** Stress-strain curves of ACM vulcanized  
**Fig. 7** Stress-strain curves of ACM/POM TPV

**Fig. 8** Mechanical properties of the ACM/POM TPV composites.

Fig 8 summarizes the variation of physical and mechanical properties of ACM/POM TPV with different Ca(OH)$_2$ dosages. The hardness of TPV is increased with the increase in Ca(OH)$_2$ dosage, which is mainly caused by the ionic clusters formed during the crosslinking of ACM, and the ionic clusters are not destroyed under smaller deformation and can resist stronger stresses. However, contrary to the pattern of hardness, the tensile strength of TPV decreases with increasing Ca(OH)$_2$ dosage, and it is the phase distribution of the two phases that has a greater effect on the strength at larger deformations. POM is a brittle plastic, and the sensitivity of the gap is very strong. Once the material has a more obvious stress concentration, it will fracture. At a lower crosslinking degree of ACM, the phase of rubber particles formed
by dynamic vulcanization crushing is smaller and more uniformly dispersed. The smaller modulus difference also makes the phase interface between the two phases more blurred, which effectively reduces the stress concentration inside the compound and results in higher tensile strength.\textsuperscript{[24]} The elongation at break of TPV fluctuates around 300\%, and the 3 min permanent deformation after tearing is similar to the fluctuation pattern of the elongation at break.

**Tensile retraction performance**

In the study of ACM pure rubber, it was found that the tearing permanent deformation of ion-bonded system and covalent bonded system after tensile fracture differed greatly; the tearing permanent deformation of ACM vulcanized by HMDC was 20~25\%, while the tearing permanent deformation of ACM vulcanized by Ca(OH)\textsubscript{2} was as high as 60~70\%. Two repeated tensile curves were tested for two specimens of HMDC 1.2phr and Ca6 with similar crosslink density at 300\% deformation variation, as shown in Fig 9. The area enclosed by the tensile retraction curve means that the energy lost in the stretching process ($W$), and the ratio ($REL$) of the energy required for the stretching process ($W_0$) characterize the resilience; the smaller the $REL$, the better the resilience. It is obvious that the energy loss of the ACM vulcanized by Ca(OH)\textsubscript{2} in the first stretching cycle is very high, more than double compared to the HMDC system, and the relative value of energy loss $REL$ is also as high as 73.15\%, which is higher than 56.8\% for the HMDC system. This indicates that the ion clusters formed by the multiple ion pairs are more significantly restricted to the surrounding molecular chains and that the ion clusters are easily destroyed during the stretching process and are difficult to recover in a short period of time, showing a huge energy loss. The cross-linked network without recovery also makes the $REL$ of the second cycle of stretching almost the same for both networks.
Fig. 10 Tensile retraction performance of ACM/POM TPV (a) First cycle (b) Second cycle

So how does the difference in energy loss of the dispersed phases of different vulcanization systems during the stretching process manifest itself in TPV? Fig 10 shows the effect of different crosslinking networks and the degree of crosslinking on the tensile retraction performance of TPV, where the permanent deformation is the remaining strain after each tensile retraction when the stress is 0%. Compared with the tensile retraction curves of ACM, the curves of different cross-linked networks of
TPV only have slight differences in the tensile process, which show their respective tensile properties, respectively, and are closer in stress values, while almost no gap arises in the retraction curve curves. After calculation, the REL of TPV with ionic cross-linked network was slightly higher than that of covalent cross-linked network in the first cycle, and slightly lower in the second cycle instead. With the increase of Ca(OH)\textsubscript{2} dosage, the REL of TPV slightly decreased, and the decrease of permanent deformation was more significant; the permanent deformation after the first tensile cycle decreased from 34.57% to 22.53%, and the permanent deformation after the second cycle decreased from 38.80% to 24.84%. The increase of disperse phase crosslinking can effectively improve the TPV plastic phase with large permanent deformation and poor elasticity. The increase in disperse phase crosslinking can effectively improve the problems of large permanent deformation and poor elasticity of TPV plastic phase.

**Heat resistant oxygen and hot oil aging properties**

![Fig. 11 Changes in physical and mechanical properties of TPVS after aging](image)

Fig. 11 Changes in physical and mechanical properties of TPVS after aging

(a) Tensile strength and its rate of change (b) Elongation at break and its rate of change

<table>
<thead>
<tr>
<th>Number</th>
<th>POM</th>
<th>TCa4</th>
<th>TCa5</th>
<th>TCa6</th>
<th>TCa7</th>
<th>TCa8</th>
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<td>0.07</td>
<td>0.27</td>
<td>0.29</td>
<td>0.62</td>
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<tr>
<td>Rate of mass change/%</td>
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<td>0.27</td>
<td>0.31</td>
<td>0.35</td>
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</tbody>
</table>
The regular structure and high crystallinity of POM can effectively reduce the chain breakage under thermal oxygen conditions, and at the same time, reduce the intrusion of solvents. The presence of ACM containing polar ester groups can form thermoplastic vulcanizates with better heat and oil resistance. Fig 11 shows the physical and mechanical properties of ACM/POM TPV and its rate of change after aging in hot air at 100 °C and 46°液压 oil at 100 °C. Compared with before aging, TPV after both hot air aging and hot oil aging showed an increase in tensile strength and a decrease in elongation at break. At high temperatures, the residual Ca\(^{2+}\) ions continue to react with the carboxyl groups of ACM, the degree of sulfation continues to increase, the tensile strength rises, and the increase in the modulus of ACM also causes it to form stress concentrations more easily in the matrix. With the increase in Ca(OH)\(_2\) dosage, the change of tensile strength after thermal oxygen aging fluctuates from 20 to 40%, and after hot oil aging, it fluctuates from 5 to 20%, while the tearing elongation is showing a decreasing trend. To confirm this, the mass volume change rates of pure POM and TCa4~TCa8 after aging in hot oil were tested, and the results are shown in Table 2. Pure POM received less erosion in hot oil, TPV showed an increase in mass and volume, and the rate of change of mass and volume gradually increased with increasing Ca(OH)\(_2\) dosage, indicating the intrusion of hot oil, which can be illustrated by combining with the later characterization of two-phase phase domains. Taken together, the TPV has better thermal oxygen and thermal oil aging properties at a Ca(OH)\(_2\) dosage of 4 parts.

**Dynamic mechanical property**

To analyze the effect of the change of crosslinking network type and degree of crosslinking on the viscoelasticity of ACM and ACM/POM TPV, a shear strain temperature scan was performed, and Fig 12 shows the variation of energy storage modulus (\(G'\)), loss modulus (\(G''\)) and loss factor (tan\(\delta\)) of ACM pure adhesive with temperature.
The rotation angle of the shear test is 0.5°, the deformation variable is smaller, and at this time the ionic clusters in the ionic crosslinked network are not destroyed and can resist greater shear stress, so the ACM after Ca(OH)$_2$ vulcanization shows higher $G'$, and with the increase of the amount of vulcanizing agent, the change of $G'$ corresponds to the change law of cross-linked density, the higher cross-linked bond density restricts the movement of molecular chains, so $G'$ is higher. For $G''$, the loss of the ionic crosslinking network is greater, and the hysteresis of the molecular chain for deformation is more obvious. On the other hand, with the change in temperature, ACM with different crosslinking bonds and crosslinking densities have different sensitivity to temperature. When covalent bonds are crosslinked, ACM gradually softens with the increase in temperature, and the resistance to shear force is weakened, and $G'$ slightly decreases; meanwhile, the motility of molecular chain segments is enhanced, and the hysteresis of chain segments is weakened, but there is no breakage of crosslinked bonds, so $G''$ and $\tan \delta$ decreases, and both changes are more in line with the regularity of conventional vulcanizates. In contrast, the ion-bonded crosslinked ACM vulcanizates exhibit great temperature sensitivity, with $G'$
decreasing by more than 40% from 65°C to 185°C, and the vulcanizates also exhibit a more paradoxical $G''$ increase in the temperature range of 95°C to 155°C, and $\tan \delta$ appears to rise across this temperature range indicating that the ion-cross-linked bonds break down under the action of temperature, leading to slippage between molecular chains and an increase in the viscosity of the material.

Fig. 13 Dynamic mechanical property of ACM/POM TPV

Fig 13 shows the dynamic mechanical properties of ACM/POM TPV, where the softening of the POM phase causes a gradual decrease in $G'$ and $G''$ of the TPV during the temperature increase from 65°C to 140°C. The $G'$ of both TPVs with different crosslinked bonds decreases linearly, but since the $G''$ of the ACM phase from 95°C to 140°C is on an increasing trend, the $G'$ of TPV in this temperature interval does not decrease linearly, and the rate of decrease is gradually slowing down, showing a higher hysteresis. When the temperature increases from 140°C to 155°C, the modulus of TPV shows a sudden drop because the temperature at this time reaches the melting temperature of POM, POM enters the viscous flow state, and the viscosity decreases rapidly. The modulus did not change much after the temperature exceeded 155°C. On the other hand, the increase in the amount of Ca(OH)$_2$ increased the $G'$ and decreased
the $G''$ of TPV. The increase in the degree of entanglement of the ACM molecular chain network increases the reversible deformation under shear and makes it more elastic, so $G'$ rises. Above the heat deformation temperature of POM, the degree of ACM crosslinking has almost no effect on the modulus of TPV, indicating that above the heat deformation temperature, the slip between the macromolecular chains of POM starts to occur, and the shear stresses suffered cannot be transferred to the rubber phase, but are all converted into deformation. The rise in $\tan\delta$ of TPV in the ionic crosslinked system is more pronounced compared to TH1.2, which further confirms the destructive effect of temperature on ionic clusters.

**Scanning electron microscope (SEM)**

Fig 14 shows the ACM/POM TPV using 4 and 6 parts of Ca(OH)$_2$. It can be seen that the different degrees of crosslinking of ACM caused the TPV to form different phase structures. The low degree of crosslinking of ACM resulted in dramatic shear fragmentation during dynamic vulcanization, wanting to form smaller rubber particles with a size of 5-10 μm. And due to the lower viscosity difference between the continuous phase of ACM and POM with low crosslinking degree, the two phases are more tightly bonded, the cross section is rougher, and tensile fracture of ACM is observed. When the degree of ACM crosslinking is larger, the ACM is difficult to break and the island phase phase domains formed are larger,\textsuperscript{[25]} and at 8-12 μm, the island phase formed is not obvious. Due to the large modulus difference between the two phases and the thin interfacial layer between the two phases, during the process of brittle fracture, large pieces of ACM are disconnected, while the rubber particles with smaller particle sizes fall off from the surface and form a large number of holes due to the weak bonding with the continuous phase of POM.
ACM was crosslinked with a metal ion vulcanization system completely different from the conventional covalent bonding vulcanization system, and acrylate rubber (ACM)/polyoxymethylene (POM) TPVs were prepared by dynamic total vulcanization technique. The amount of Ca(OH)$_2$ in ACM was varied, so as to change the modulus of ACM during the dynamic vulcanization of TPVs, and the effect of the difference in modulus between the two phases on the phase state of TPVs was investigated. Comparing with the covalently bonded system after vulcanization of HMDC and analyzing the connection between properties and structure, the following conclusions were obtained: Ca$^{2+}$ can form metal ion bonds with -COOH of ACM and
form ion clusters with each other to vulcanize ACM. Compared with the conventional covalent bonding system, the TPV under ionic bonding can improve the stretching stress below 100% deformation by up to 31%, the elongation at break by 14.5%, exhibit higher permanent deformation after stretching, higher energy storage modulus, and slower decrease in the loss modulus in the interval of 95~140°C. With the increase of Ca(OH)₂ dosage, the crosslink density of ACM gradually increases and decreases at 8 phr. The increase of disperse phase modulus increases the phase domain of the disperse phase, weakens the bond with the matrix, weakens the tensile strength, increases the intrusion of hot oxygen and hot oil received during aging, increases the energy storage modulus, and decreases the loss modulus.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Reference**


[22] Y. Huang, M. Qi, W. Pang, G. Si, C. Tan, Polymer. 2022, 259, 125328.


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