

Adhesive and viscoelastic performance of surface functionalized nano-Fe₃O₄ induced orientated ethylene vinyl-acetate composite hot melt adhesives

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ABSTRACT: Different surface functionalized Fe₃O₄ were added to ethylene vinyl-acetate copolymers (EVA) composite hot melt adhesives (HMAs) to study their influence on the properties of composite HMAs. The adhesion and viscoelastic properties for HMAs were studied using an electromechanical universal testing machine, dynamic mechanical analyzer (DMA) and parallel-plate rheometer, respectively. Orientation structure of HMAs was studied by Infrared dichroism. The results showed that tetraethoxysilane (TEOS) treated Fe₃O₄ showed better compatibility with EVA composite HMAs, and that TEOS-treated Fe₃O₄/EVA composite HMAs presented better adhesion property and processing fluidity, compared with bare Fe₃O₄/EVA composite HMAs and silane coupling agent KH560 treated Fe₃O₄/EVA composite HMAs. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43931.

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INTRODUCTION

As the development of environmental friendly adhesives, hot-melt adhesives (HMAs) are increasingly important.^{1–3} Due to the wide range of melt index values, vinyl acetate content and superior adhesion ability to a variety of materials, ethylene vinyl acetate (EVA) copolymers have become the most widely used raw materials for HMAs.⁴ EVA copolymers both have nonpolar polyethylene (PE) chain segments and polar polyvinyl acetate (VA group) chain segment, which make EVA molecular has strong nonpolar interaction with PE molecular and polar interaction with steel pipeline of oil transport. Meanwhile, it tends to form chemical bonds or electrical double layers in the contact surface between EVA composite HMAs and steel pipeline.⁵ Therefore, EVA composite HMAs have the ability to adhesion with both nonpolar PE and polar steel pipeline at the same time, and are widely used in anti-corrosion of pipeline.^{6–8}

However, due to the weak adhesion strength, bad processing fluidity, and poor coating wettability, traditional EVA composite HMAs cannot meet the industry standard of pipeline corrosion protection. Various kinds of methods have been applied to modify EVA composite HMAs, for example, adding elastomers and multiple blending. Nowadays, inorganic magnetic nanoparticles (MNPs) as a kind of new materials have better application

prospects in many fields due to its unique structure and magnetic properties.^{9–11} Adding MNPs to polymer matrix can obtain excellent structure, organization, and performance.

In our previous studies,^{12–14} we first added magnetic nanoparticles Fe₃O₄ to EVA composite HMAs and got a composite HMAs with good adhesion properties, processing fluidity and high segments orientation degree. Surface treated Fe₃O₄ by different ways were also studied to modify EVA composite HMAs in our previous study.¹⁵ However, our previous studies showed that adhesion properties of Fe₃O₄ modified EVA composite HMAs were improved, but still not reached the ideal values.

In this study, to further improve the effect of Fe₃O₄ on adhesion and viscoelastic properties of EVA composite HMAs, Fe₃O₄ were surface functionalized by tetraethoxysilane (TEOS) and silane coupling agent KH560 respectively. The adhesion and viscoelastic properties for HMAs were studied using an electromechanical universal testing machine, dynamic mechanical analyzer (DMA), and parallel-plate rheometer, respectively. Infrared dichroism was used for studying orientation structure of HMAs. In addition, the effect of particles content on mechanical properties, adhesion properties, orientation degree, and viscoelastic properties was also studied.

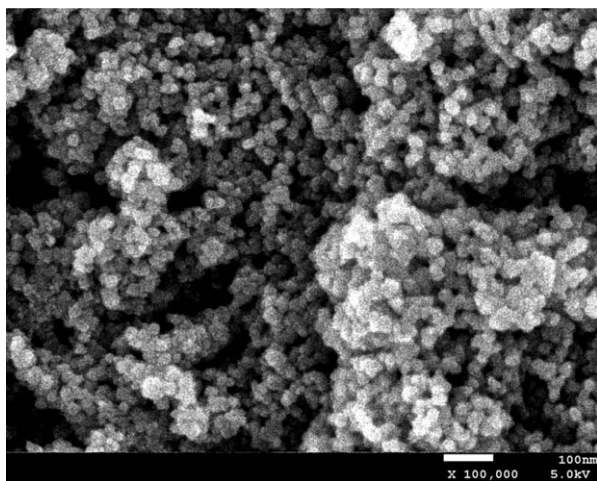


Figure 1. Scanning electron microscopy (SEM) image of prepared Fe_3O_4 MNPs.

EXPERIMENTAL

Materials

EVA (28% VA content) block copolymer (industrial grade) was purchased from HONAM Petrochemical Corp., South Korea. Rosin (industrial grade), paraffin wax (industrial grade), ethanol (AR), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, AR), sodium hydroxide (NaOH, AR), iron chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, AR), and tetraethoxysilane (TEOS, AR) were all bought from Chendu Kelong Chemical Factory, People's Republic of China. EVA (VA content was 28%) grafted maleic anhydride (EVA-g-MAH, industrial grade) was brought from Guangzhou Synthesis Chemical Factory, People's Republic of China. Polyvinyl alcohol 0588 (PVA0588, industrial grade) was supplied by Sichuan Vinylon, Sinopec, Ltd., Co. The purity water was prepared by the Water Purification System (UPZGK, Chengdu Ultrapure Technology Co., Ltd., People's Republic of China). Silane coupling agents (ethyl trimethoxysilane, KH560) was bought from Nanjing Daoning chemical co., Ltd, People's Republic of China. The EVA copolymer herein had low and widely distributed molecular weight measured by GPC ($M_w = 7.43 \times 10^4$ g/mol, $M_n = 2.72 \times 10^4$ g/mol, $M_w/M_n = 2.73$).

Methods

Synthesis of Fe_3O_4 Magnetic Nanoparticles (MNPs). The Fe_3O_4 nanoparticles were synthesized by the procedure reported previously in ref. 10. The polyvinyl alcohol emulsion as the reaction medium can improve the dispersion effect of magnetic particles. Briefly, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved in PVA0588 solution of 1 wt % to prepare the mixed solution of iron ion with 2:1 molar ratio of Fe^3 to Fe^{2+} , then 100 mL mixed solution of iron ion was dropped slowly to 300 mL NaOH solution of 0.4 mol/L through a constant pressure drop funnel at 80 °C in water bath, and reacted for 1 hour with the agitation speed at 600 rad/min under nitrogen protection. The black precipitates were separated using a permanent magnet and washed several times with deionized water and ethanol after cooling to room temperature. Scanning electron microscope (SEM) image of the synthetic MNPs (Figure 1) showed a polydisperse sphere morphology with a wide particle size distribution at 20–30 nm.

Surface Modification of Fe_3O_4 Nanoparticles. TEOS can be hydrolyzed easily in water to generate SiO_2 . The preparation process of silica-coated MNPs (MNPs-TEOS) was that, dispersing the prepared Fe_3O_4 particles (20 g) in 250 mL ethanol through ultrasonic dispersion for 20 minutes, then adding 100 mL TEOS to the above solution under alkaline environment (pH 12) and nitrogen protection with stirring speed of 400 rpm at 50 °C and reacting for 1 h. The prepared MNPs-TEOS particles were washed thoroughly with ethanol and collected by an external permanent magnet. Finally, particles were dried at 60 °C in vacuum drying oven for 24 h. The KH560 surface modified method was used by Ref. 15. Briefly, dispersing 10 g Fe_3O_4 particles in 250 mL dispersant (volume ratio of ethanol to water is 3:2) by ultrasonic vibration for 30 minutes, then adding 5 mL KH560 to the solution and preheating at 30 °C water bath for 10 minutes in three-necked bottle. The reaction was conducted at 50 °C with 500 rpm stirring for 2 h under nitrogen atmosphere. After allowing the solution to cool naturally, functionalized Fe_3O_4 particles were isolated by an external permanent magnet and dried at 40 °C in a vacuum drying for 72 h.

Preparation of Composite Hot Melt Adhesives. EVA/nano- Fe_3O_4 particles composite hot melt adhesives was made up of EVA/nano- Fe_3O_4 composites, rosin and paraffin wax. The contents of EVA, rosin and paraffin wax were 100, 50, and 20 phr, but the MNPs contents varied from 0, 5, 10, 15, 20 phr to 25 phr. The preparation methods of composite adhesives were reported at our previous study.^{12,15} Furthermore, the peel test samples were made by the following method, firstly spreading the composite hot melt adhesives on a PE layer made by cutting PE heat shrinkable tape into specific shape, and then using it to stick iron layer when the adhesives was still molten, lastly the samples were pressed by a vulcanizing press under 1 MPa pressure at 60 °C for 2 h and then cooled normally. All the test samples should process at one time for the same thermal stress history. The tensile test samples were made by compression molding on a vulcanizing press.

Characterization

Thermogravimetry Analysis (TGA). The particles with different modifications were tested by TGA (TGA/SDTA85°, Mettler Toledo Corp., Ltd., Switzerland) under N_2 protection. Test temperature range was 25–500 °C and heating rate was 10 °C/min.

Vibrating Sample Magnetometer (VSM). The saturated magnetic strengths of particles were measured by VSM, (BKT-4500Z, Quantum Design Ltd, The United States) in open circuit mode at normal temperature.

Scanning Electron Microscopy (SEM). Nano- Fe_3O_4 particle was observed by SEM (JSM-7500F, Japan Electron Optics Laboratory Corp., Ltd., Japan). The adhesion fracture surface of EVA composite HMAs was also observed by this instrument after metal spraying treatment.

Gel Permeation Chromatography (GPC). The molecular weight and distribution of EVA were measured by GPC (Viscotek RImax, Malvern Instruments Ltd, Britain) at 40 °C with tetrahydrofuran as dissolvent.

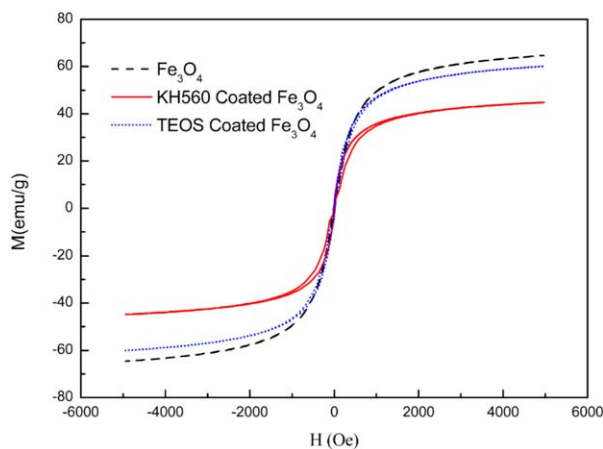


Figure 2. Magnetization curves of MNPs, MNPs-TEOS, and MNPs-KH560 at 25 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Orientation Degree Test. The orientation degree of EVA copolymer in adhesives was measured by infrared dichroism (Nicolet 6700, Thermo Fisher Scientific Corp., Ltd., The United States). The samples were 10 μm thick, and the scan range of wave number was from 4000 to 500 cm^{-1} and the scan times was 32. The tested angle was at (0°, 90°), (10°, 100°), (20°, 110°), (30°, 120°) and (40°, 130°). The rate value R of the infrared dichroism can be obtained through the polarized angle α , and the orientation degree f and relative degree f' could be obtained,¹⁶ respectively, by eqs. (1) and (2).

$$f = \frac{R-1}{R+2} \times \frac{2}{3\cos^2\alpha - 1} \quad (1)$$

$$f' = \frac{R-1}{R+2} \quad (2)$$

Viscoelastic Properties Test of HMAs. Viscoelastic properties of the HMAs were characterized by dynamic mechanical analysis equipment (DMAQ800, TA Corp., Ltd., The United States) at a frequency of 1 Hz. The dimensions of samples used for this study was 50 mm \times 12 mm \times 3 mm, and the test temperature was in the range of -80°C to 40°C with a heating rate of $3^\circ\text{C}/\text{min}$ under liquid nitrogen in a dual cantilever mode. Parallel-plate rheometer (Bohlin Gemini 200, Malvern Instruments Ltd., Britain) was also used to investigate the viscoelastic properties under 75°C , and the shear rate of steady model ranged from 0.01 to 100 s^{-1} and the frequency range of dynamic model was 0.01–100 Hz.

Mechanical Properties Measurements. The peel test was undertaken on an electromechanical universal testing machine [MT6104, Mechanical Testing & Simulation Systems (China), Corp., Ltd.] with the standard of GB/T2790-1995 at room temperature (25°C), and peel rate was 200 mm/min. The tensile test was undertaken on the same machine with the standard of GB/T528-2009 at 25°C , and the tensile rate was 100 mm/min. The tests were retested 4 times and made the average value to make sure that the error distribution of the experimental data was acceptable in the mechanical properties test.

RESULTS AND DISCUSSION

Magnetic Particles Properties Analysis

The magnetic properties of bare and surface coated MNPs were characterized by vibrating sample magnetometer at 25°C . The results (Figure 2) showed that bare Fe_3O_4 MNPs presented the highest magnetization which decreased after surface functionalization, and MNPs-TEOS and MNPs-KH560 showed the lowest magnetization in response to the applied magnetic field. The results were in accord with the observations reported in the literature, regarding the decrease in magnetization for thicker surface coatings.¹⁷ The reason why magnetic particles magnetization declines after surface modification is that the coating layer of SiO_2 generated by TEOS and the polymer film on the surface slightly weakened the MNPs magnetization in the process of TEOS and KH560 modifying Fe_3O_4 particles.

The TGA curves (Figure 3) reflected that the amount of weight retention for bare Fe_3O_4 was basically at 100%, however, the weight loss of MNPs-TEOS and MNPs-KH560 increased with the temperature increasing. The weight remain of MNPs-KH560 was approximately 95% due to the degradation of the KH560 organic coating on the Fe_3O_4 not the degradation of Fe_3O_4 at higher temperature. The results showed a substantially higher density of surface functional groups for KH560 coated Fe_3O_4 particles than MNPs-TEOS. From another point of view, the Fe_3O_4 particles were successfully functionalized by KH560 and TEOS.

Mechanical Properties Analysis of Composite

Hot Melt Adhesives

The tensile test results (Figure 4) showed that the tensile strength of bare MNPs/EVA composite HMAs was approximately 2.5 MPa and the elongation at break reached 295%. However, the tensile strength of functionalized MNPs-TEOS/EVA composite HMAs increased with the content of magnetic particles increasing until to 15 phr, but decreased when it surpassed 15 phr, and the tensile strength presented the maximum value of 4.2 MPa and the elongation reached 600% at 15 phr. The elongation of MNPs-TEOS/EVA composite HMAs at break was significantly higher than that of unmodified EVA

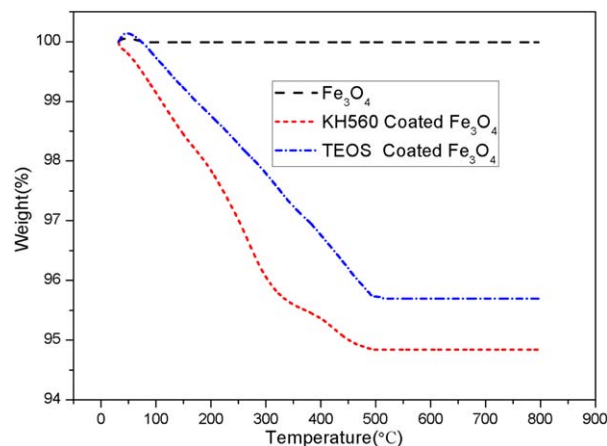


Figure 3. TGA curves of MNPs, MNPs-TEOS, and MNPs-KH560. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

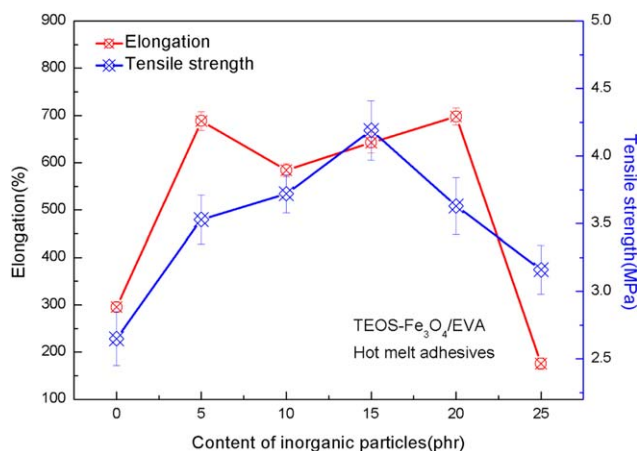


Figure 4. Tensile strength curves of different content of MNPs-TEOS/EVA composite HMAs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

composite HMAs. The stretching process of HMAs presented the featured yielding and thin neck cold drawn of polymer. The above phenomenon was attributed to the interaction of MNPs with the molecular chain of polymer matrix in the interface layer, which formed a three-dimensional network structure, and nanoparticles played an important role as the physical crossing points.¹⁸ The increased tensile strength could be due to the increased segments orientation degree in Figure 8.

The result (Figure 5) of U-shape peel strength test for composite HMAs at 25 °C showed that the peel strength of both the bare MNPs/EVA and functionalized MNPs/EVA composite HMAs increased with the content of nanoparticles increasing, and reached the maximum value when particles amount accounted for 15–20 phr. However, the peel strength of functionalized MNPs/EVA composite HMAs was greatly increased by the modifier of nanoparticles, especially by TEOS. MNPs/EVA HMAs presented excellent bonding performance to the steel pipe due to that the metal material had strong polar interaction with VA group on the surface, which could be reinforced

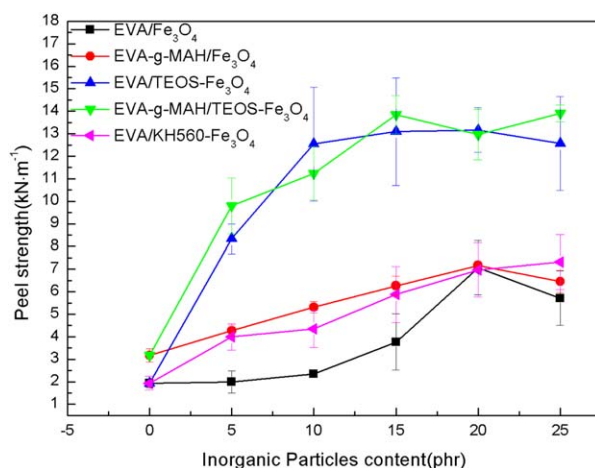


Figure 5. Curves of U-shape peel strength for composite HMAs with different kinds and content of MNPs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

by the formation of orientation structure of VA segments when induced by magnetic particles. MNPs-TEOS dispersed better in HMAs compared with bare MNPs (Figure 6). This better compatibility made more Fe₃O₄ particles move to the interface of adhesives with steel pipeline, and increases segments orientation degree. As a result, bonding strength (peel strength) is improved, due to the reinforced magnetic interaction between Fe₃O₄ particles and steel pipeline. In addition, increased orientation degree (Figure 8) can also improve bonding strength (peel strength), due to the reinforced polar interaction between polar VA segments and steel pipeline. Therefore, MNPs-TEOS modified EVA composite HMAs had better bonding strength. Wu⁶ investigated EVA grafted maleic anhydride (MAH) (EVA-g-MAH) and found that the peel strength increased a lot by introducing polar groups MAH, but the glass transition temperature (T_g) was higher and the flow properties was worse than EVA HMAs. In view of this, MNPs were used to modify both EVA and EVA-g-MAH to obtain composite HMAs in this paper. The results (Figure 5) showed that the peel strength of EVA/Fe₃O₄

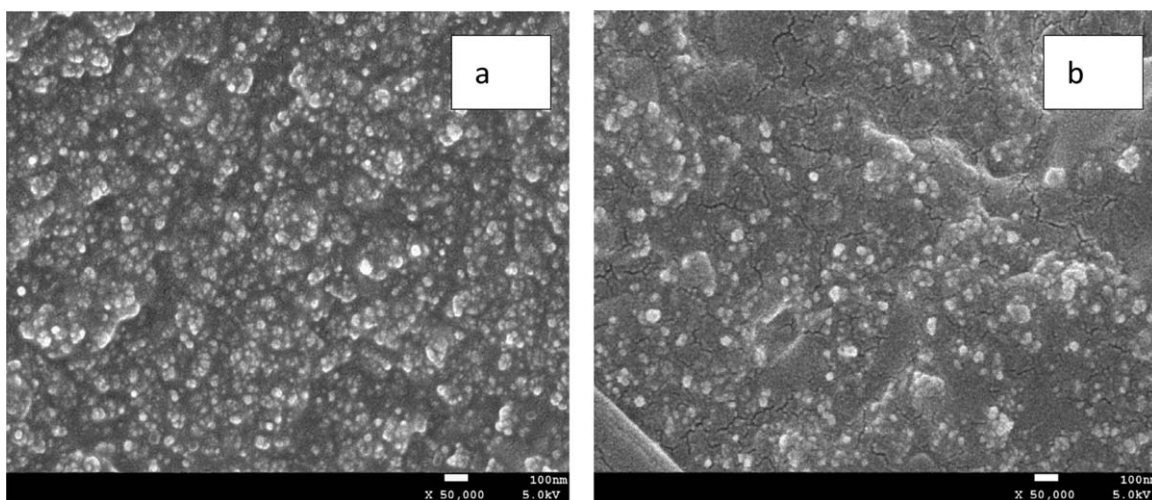


Figure 6. SEM micrographs of the freeze fractured surface of composite HMAs with different MNPs before mechanical properties testing (a), Fe₃O₄ MNPs; (b) TEOS Functionalized Fe₃O₄ MNPs.

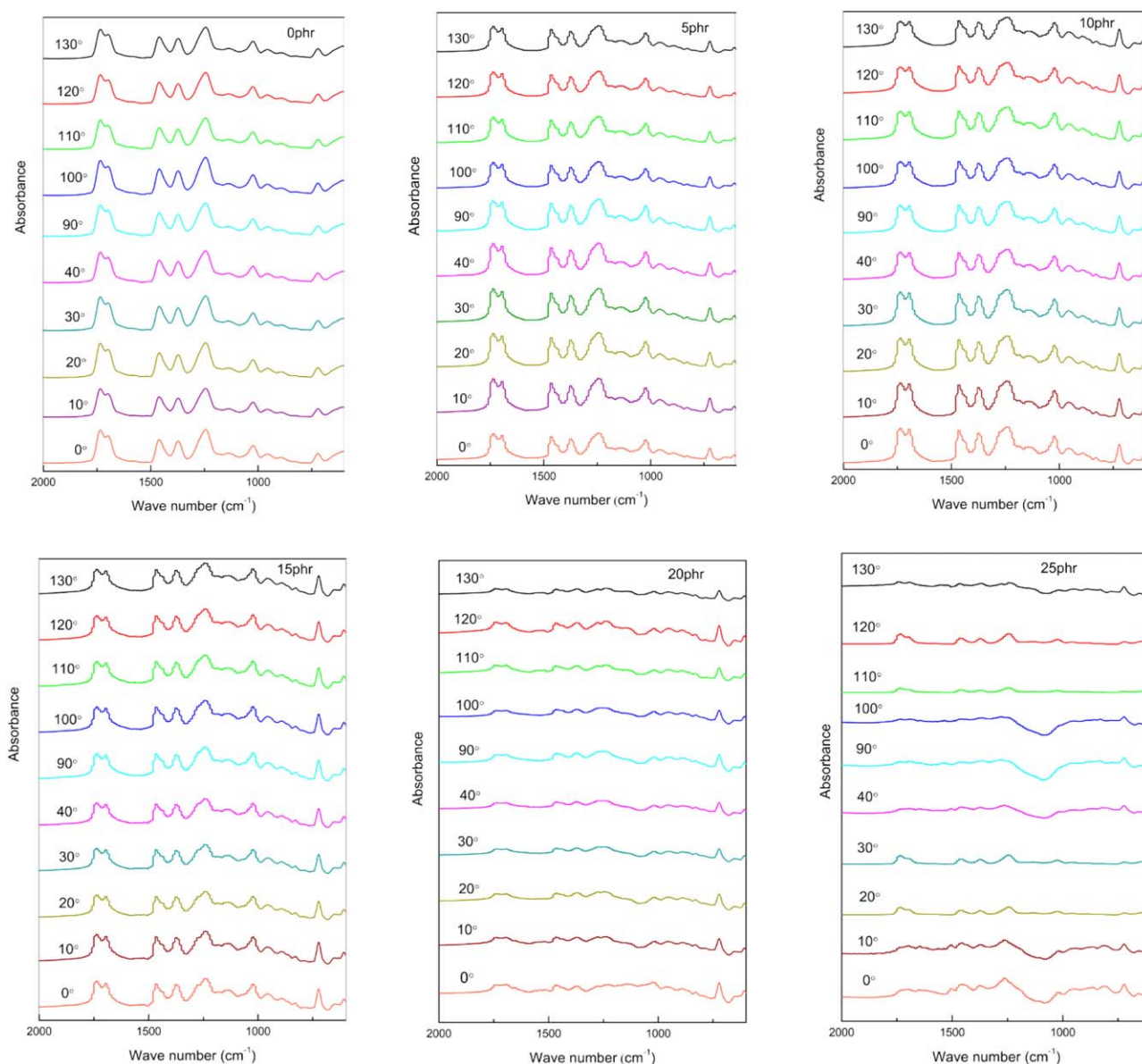


Figure 7. Infrared dichroism spectrogram of EVA composite HMAs with different content of MNPs-TEOS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

composite HMAs was much lower than that of EVA-g-MAH/ Fe_3O_4 composite HMAs, and the peel strength of EVA/ Fe_3O_4 -KH560 composite HMAs was basically similar to that of EVA-g-MAH composite HMAs namely 7 KN/m. However, the peel strength of EVA-g-MAH/TEOS- Fe_3O_4 and EVA/TEOS- Fe_3O_4 were very close and achieved 13 KN/m. Therefore, TEOS surface treated MNPs modified EVA composite HMAs could match with maleic anhydride grafted EVA composite HMAs in peel strength, and adding MNPs could also reduce the cost of the matrix resin.

Segments Orientation of EVA Induced by MNPs

Magnetic particles had polar interaction with both the steel tube and VA groups, therefore, VA groups would move to the steel tube and orientate under the induced action of magnetic particles. Ori-

entation movement of segments can be investigated by IR dichroism.^{19,20} It (Figure 7) showed that the peaks at $1700\text{--}1770\text{ cm}^{-1}$ and $1100\text{--}1280\text{ cm}^{-1}$ and $1140\text{--}1250\text{ cm}^{-1}$, respectively, were the stretching vibration bands of $\text{C}=\text{O}$ and $\text{C}-\text{O}-\text{C}$ and $\text{C}-\text{C}$, furthermore the peak at $1350\text{--}1490\text{ cm}^{-1}$ was the in-plane bending vibration peak of $\text{C}-\text{H}$ of CH_3 group. In this paper the main groups ($\text{C}=\text{O}$, $\text{C}-\text{O}-\text{C}$, $\text{C}-\text{C}$, CH_3) which the absorption band were at $1700\text{--}1770\text{ cm}^{-1}$, $1100\text{--}1280\text{ cm}^{-1}$, $1140\text{--}1250\text{ cm}^{-1}$, and $1350\text{--}1490\text{ cm}^{-1}$, respectively, were selected to research the orientation property. The result (Figure 8) showed that the relative orientation degree of main groups ($\text{C}=\text{O}$, $\text{C}-\text{O}-\text{C}$, $\text{C}-\text{C}$, CH_3) in EVA molecules increased with the content of MNPs-TEOS increasing, thus the orientation effect of VA groups was enhanced by adding MNPs-TEOS. Relative orientation degree of $\text{C}=\text{O}$ and CH_3 groups of VA segments surpassed 20% when the amount of

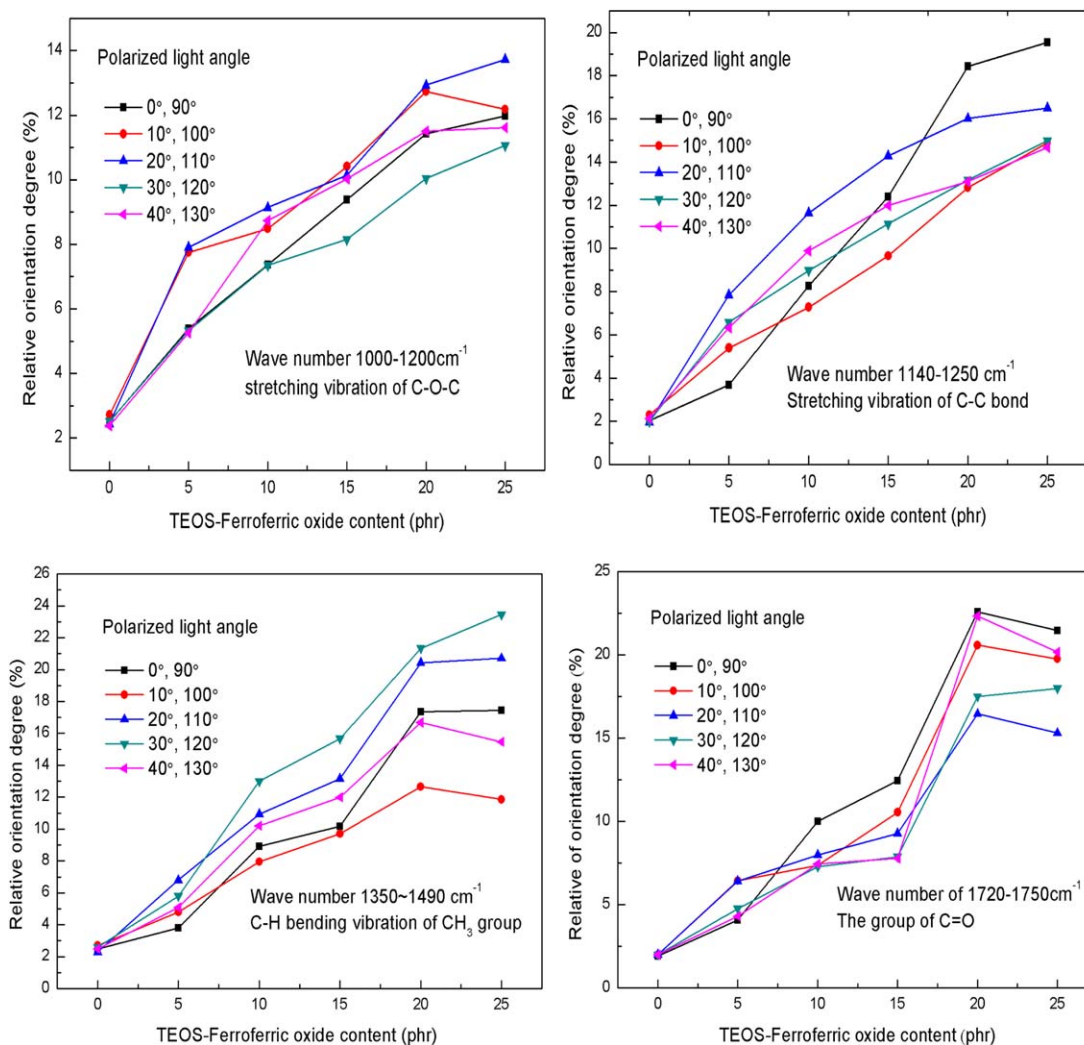


Figure 8. Relative orientation degree of functional groups with different content of Fe₃O₄-TEOS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

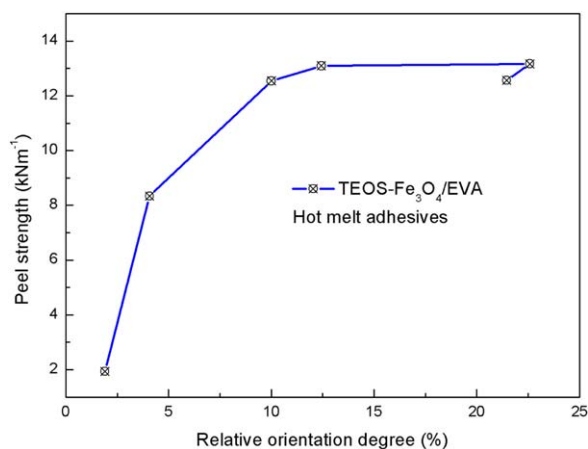


Figure 9. The relationship of peel strength with relative orientation degree of MNPs-TEOS/EVA HMAs [test angle, (0, 90°), MNPs-TEOS content, 15 phr]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

particles rose to 20–25 phr. The orientation movement of VA groups under the induced action of MNPs will inevitably induce rearrangement of segments and change the molecular conformation, which can make more VA groups of EVA molecular chain move to the interface of steel, then affect the bonding properties of the adhesive. The peel strength increased with the relative orientation degree increasing (Figure 9), which showed that the orientation movement of VA groups to the interface of steel could improve the bonding strength.

The relative orientation degree of MNPs-TEOS/EVA HMAs increased rapidly and surpassed 20% when adding particles to 10 phr, however, the relative orientation degree of MNPs-KH560/EVA HMAs changed little and basically no more than 10% with the content increasing of MNPs (Table I). This could be attributed to that MNPs-TEOS had better compatibility and stronger polar interaction with EVA resin matrix (especially the VA groups) than MNPs-KH560, which reinforced the movement of particles to the surface of steel tube and made more VA segments form the orientation structure.

Table I. Relative Orientation Degree of Some Function Group for Different Surface Treated MNPs/EVA HMAs with Different Contents of Particles at the Tested Angle of (0, 90°)

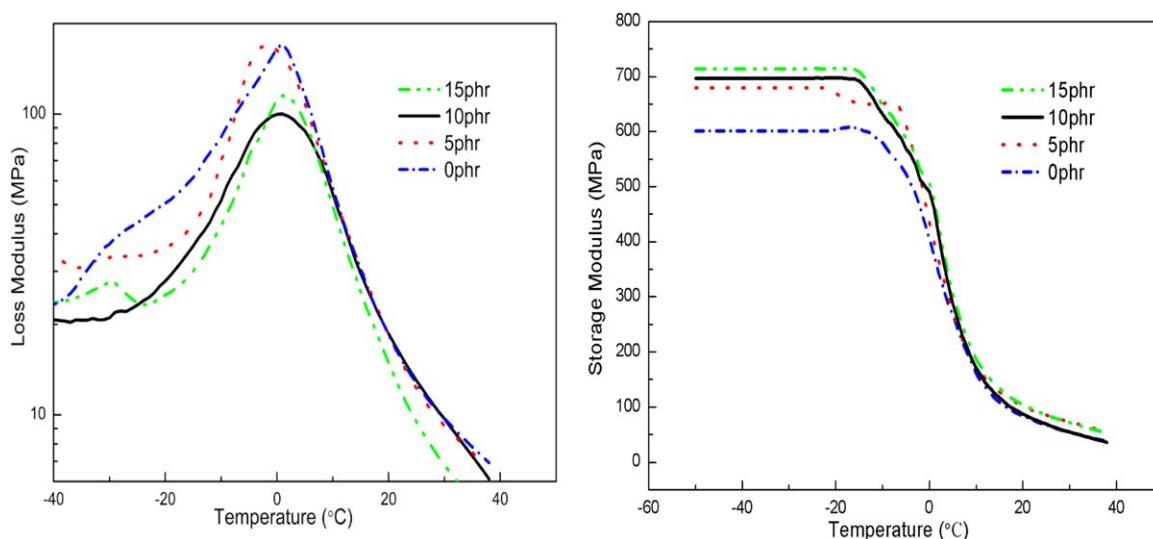
Group	C=O		C—O—C		CH ₃		C—C	
	KH560	TEOS	KH560	TEOS	KH560	TEOS	KH560	TEOS
5 phr	5.2	4.7	5.6	5.4	5.8	3.8	6.4	3.7
10 phr	5.6	10.0	6.5	7.4	6.9	8.9	7.0	8.3
15 phr	6.8	12.4	7.4	9.4	7.3	10.2	7.8	12.4
20 phr	7.4	22.6	7.9	11.4	7.8	17.4	8.4	18.4
25 phr	7.8	21.4	8.7	12.0	8.2	17.4	8.2	19.5

Dynamic Mechanical Analysis (DMA) of EVA Composite Adhesives

Viscoelastic properties of polymers are greatly depended on their structure. Investigating viscoelasticity of polymers can provide not only the theoretical foundation for polymer processing and the application for mechanic performance, but also the information of molecular structure and molecular motion. The loss modulus and storage modulus of MNPs-TEOS modified EVA composite HMAs varied significantly from -10 to 10 °C (Figure 10). When adding the filling agent, for polymer filling system, the storage modulus increased, loss modulus and internal friction peak $\tan \delta$ declined greatly, but had less effect on the glass transition temperature (Figure 11). When the interaction of fillers MNPs-TEOS with the resin matrix became stronger, the MNPs could induce nucleation and crystal in the crystalline polymer substrate and make the crystallinity of interface phase higher based on the theory reported in studies.^{21–23} The storage modulus of MNPs-TEOS/EVA HMAs increased with the content of particles increasing (Figure 10), namely adding magnetic particles increased the rigidity of polymer matrix and the viscous force of HMAs. Loss modulus reflects the size of internal friction damping motion of molecular chain

segments and the complexity of molecular motion to a certain extent. Loss modulus changed obviously in the glass transition region because MNPs had strong interaction with polymer resin which reduced the alpha relaxation units of polymer and affected the movement of molecular chain segments (Figure 10). The result was consistent with the observations reported in the literature.²⁴

Researchers^{4,25,26} had investigated the effect of paraffin and tackifier on the compatibility and glass transition temperature of EVA composite HMAs by DMA, and found that paraffin wax had no effect on the glass transition temperature of the polymer system but affected the crystallization capacity of the system. The improvement of crystallinity reduced internal friction values and widened the area of internal friction peak temperature. These observations were in accord with MNPs-TEOS/EVA filling system, namely the internal friction peak slightly moved to high temperature, meanwhile, loss peak had a tendency to widen with the content of the particles increasing. These were because that the segment motion of amorphous phase of EVA HMAs in the transition zone was limited by crystalline phases and that MNPs had played an important role in physical junction for polymer matrix.

**Figure 10.** Loss modulus (E'') and storage modulus (E') versus temperature for MNPs-TEOS/EVA HMAs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

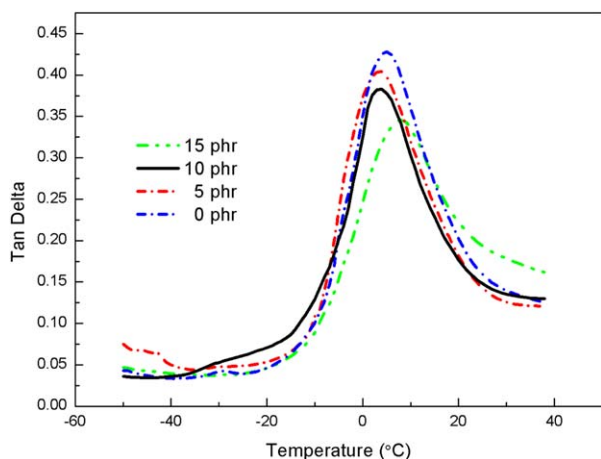


Figure 11. Tan Delta versus temperature for MNPs-TEOS/EVA HMAs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Rheological Behavior Analysis of EVA Composite Hot Melt Adhesives

Viscoelasticity properties of EVA composite HMAs have been reported by many researchers through the method of DMA,^{27–31} but studies on the viscoelasticity and the processing fluidity of hot melt adhesive performance by rheometer are still rare. The rheological property of EVA composite HMAs not only relates to the wetting ability to bonding substrate but also affects the coating performance, thereby affect the bonding performance of the steel pipe materials. The results of rheology test for functionalized MNPs/EVA HMAs showed that the elastic modulus G' and loss modulus G'' of MNPs modified EVA adhesive increased with the rise of oscillation frequency and also presented bigger modulus with the increased content of magnetic particles (Figure 12), especially MNPs-TEOS/EVA HMAs performed obviously. But the improvement of viscoelastic effect of EVA adhesives was not obvious (Figure 13) because that the

molecular chains of EVA resins were easily entanglement under melt flow state and that the ordinary filling technology was unable to solve the problem of filler dispersion. However, TEOS surface functionalized MNPs (TEOS- Fe_3O_4) had good compatibility, excellent dispersion in EVA resins (Figure 6) and strong interaction with VA groups in EVA molecular, so the chemical bonds effect of hydrogen bonding might exist. These might had affected the motion of molecular chains and made the motion of molecular chain regular, leading to the increase of viscoelasticity of EVA composite HMAs that could be illustrated by that the elastic modulus and loss modulus of functionalized MNPs EVA HMAs presented higher values than that of bare MNPs EVA hot melt adhesive.

Flow characteristics (viscosity) of HMAs at melting state are important for evaluating its adhesion and bonding properties. The relationship of the variation of apparent viscosity of MNPs/EVA composite HMAs with shear rate showed that apparent viscosity hardly changed at low shear rate for quite a long scope and had a long platform area (Figure 13), namely the shear viscosity could be considered as the zero shear viscosity of EVA HMAs, which was similar to the results reported in the study.³² The apparent viscosity of MNPs/EVA composite HMAs was bigger than that of EVA composite HMAs and increased with the content of magnetic particles increasing, meanwhile, the viscosity of MNPs/EVA composite HMAs changed more obviously with the change of shear rate at high shear rate, and HMAs presented better behavior of pseudo plastic fluid (Figure 13), which resulted in the excellent processing fluidity. As a consequence, MNPs modified EVA composite HMAs had bigger viscosity and better adhesion properties. TEOS-MNPs/EVA HMAs had excellent processing rheological property and was easy to flow, deform, and wet so as to improve the bonding strength and the anticorrosive ability of pipeline.

Relaxation time is important for all viscoelastic function and can be calculated by the loss modulus [G'' , eq. (3)] and storage modulus [G' , eq. (4)]. Ferry^{33,34} proposed that oscillatory loss

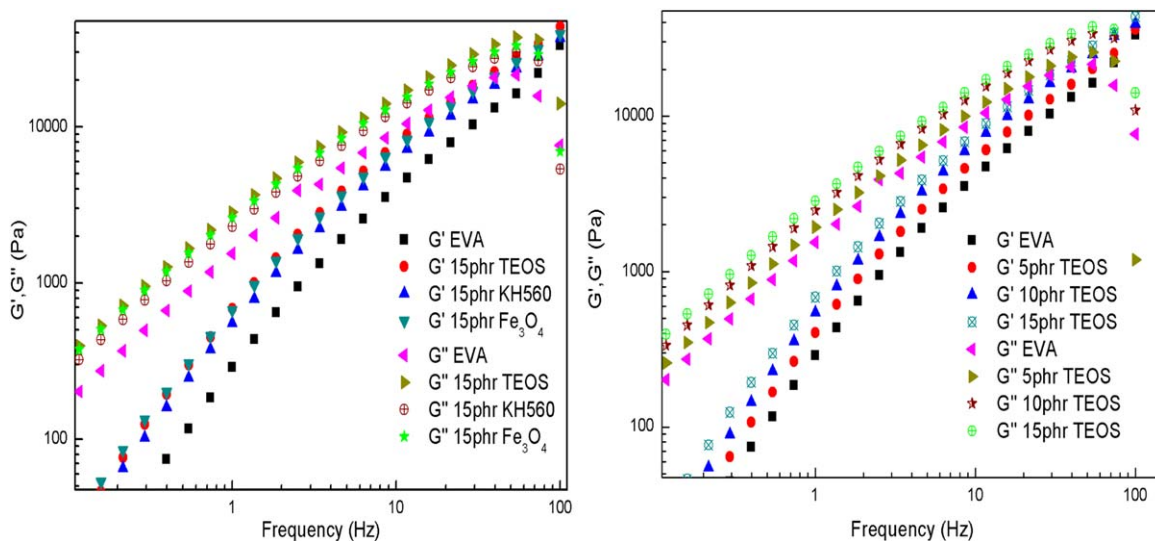


Figure 12. Storage modulus and loss modulus vs frequency for MNPs/EVA HMAs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

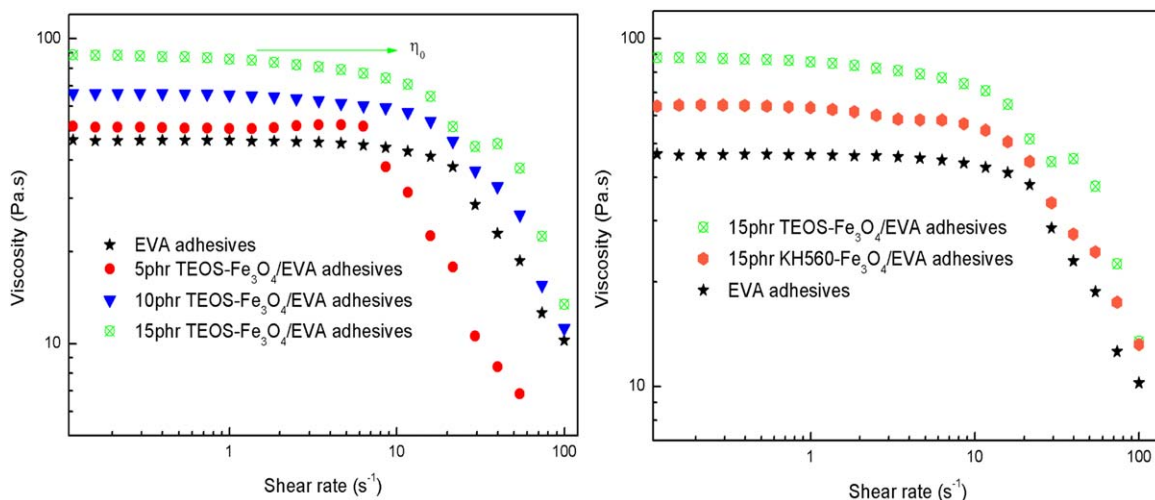


Figure 13. The relationship between viscosity and shear rate of MNPs-TEOS/EVA HMAs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

modulus could be used to calculate the approximate solution of the relaxation time by eq. (5) which only needed G' to get a second approximate solution of relaxation time spectrum.

$$G'(\omega) = \int_{-\infty}^{\infty} \frac{H(\ln \lambda) \cdot \omega^2 \lambda^2}{1 + \omega^2 \lambda^2} d \ln \lambda \quad (3)$$

$$G''(\omega) = \int_{-\infty}^{\infty} \frac{H(\ln \lambda) \cdot \omega \lambda}{1 + \omega^2 \lambda^2} d \ln \lambda \quad (4)$$

$$H_2''(\lambda) = \frac{2}{\pi} \left[G''(\omega) - \frac{dG''(\omega)}{d \ln \omega} \right] \Big|_{\sqrt{3}/\omega = \lambda} \quad (5)$$

where λ is the relaxation time, ω is the angular frequency, and $H(\lambda)$ is the relaxation modulus.

When adding MNPs to EVA composite HMAs, the relaxation time spectrum covered a wider time range (Figure 14). Meanwhile, its relaxation modulus increased with the increased content of magnetic particles at same relaxation time (Figure 14), this was mainly because that the MNPs had interaction with EVA molecular chain and that TEOS-MNPs had stronger inter-

action with VA groups which led to that the motion of EVA molecular chains was restricted. This effect led to the rearrangement and orientation of EVA molecules chain and extended the relaxation time. At the same time, the addition of MNPs increased the modulus of matrix polymer resin and improved the mechanical performance. It also showed that the relaxation time of HMAs molecular chain mainly concentrated in a very short time range of 1 second (Figure 14). This meant that EVA molecular chains could relax in a very short period and then completed the orientation movement. This further showed that in the process of HMAs coating engineering, EVA molecular chain segments had enough time to relax during the movement which led to the segments rearrangement and orientation and thus improved the bonding strength.

CONCLUSIONS

TEOS surface treated Fe_3O_4 MNPs had excellent compatibility with EVA resins and dispersed well in HMAs. Adding surface treated MNPs changed the orientation structure and improved the mechanical performance, peel strength, and rheological property of EVA composite HMAs.

When adding 15 phr MNPs-TEOS, the bulk strength of EVA composite HMAs reached 4.2 MPa and the elongation at break was up to 600%. The peel strength of MNPs-TEOS modified EVA composite HMAs reached 13 kN/m and was higher than that of MNPs-KH560 modified EVA composite HMAs (7 kN/m). Adding MNPs could also induce the EVA molecular chains to orientate, and the VA groups had a higher relative orientation degree f' which could reach 20% when the adding amount of MNPs was 20–25 phr. In addition, the peel strength also increased with the increased relative orientation degree of VA groups. As the increased content of MNPs-TEOS, the storage modulus E' of composite HMAs increased and the loss modulus E'' decreased, and the peak of internal dissipation $\tan \delta$ also decreased and slightly moved to high temperature. MNPs-TEOS modified EVA composite HMAs showed better processing fluidity than the unmodified EVA composite HMAs.

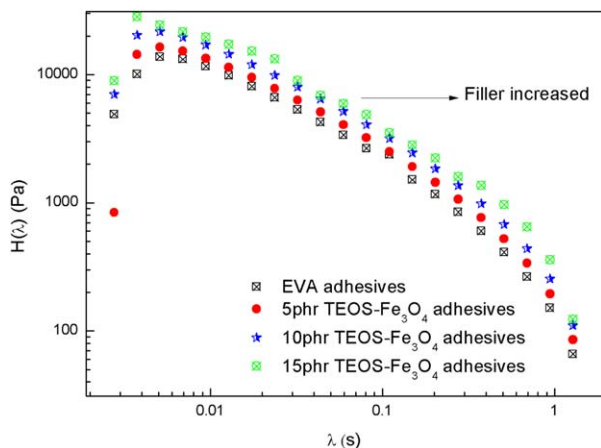


Figure 14. Relaxation modulus versus relaxation time for MNPs-TEOS/EVA HMAs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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