

# Effect of Damp-Heat Aging on the Properties of Ethylene-Vinyl Acetate Copolymer and Ethylene-Acrylic Acid Copolymer Blends

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**ABSTRACT:** The aim of this investigation is to evaluate the effect of damp-heat aging on properties of ethylene-vinyl acetate (EVA) copolymer (14 wt % vinyl acetate units), ethylene-acrylic acid (EAA) copolymer (8 wt % acrylic acid units) and their blends. Attenuated total reflection Fourier transform infrared spectrum (ATR-FTIR), differential scanning calorimeter (DSC), wide angle X-ray diffraction (WAXD), and mechanical tests are employed to investigate the changes of copolymer blends' structures and properties. ATR-FTIR tests show that increase of carbonyl index is owing to the incorporation of oxygen into the polymeric chain of EVA in the blends and has not much influence on the EAA. By DSC measurements, the low temperature endothermic peak ( $T_{m2}$ ) of various EAA/EVA blends at about 43.7°C attributed to the secondary crystallization is increased with the aging time, which means the lamellar thickness of low temperature crystallite is increased. The increase of low tempera-

ture peaks probably derives from the interphase or even amorphous parts of both EVA and EAA components. The crystalline size detected by WAXD and degree of crystalline have both been improved by damp-heat aging. By mechanical tests, the sample has more hardness, more modulus at 100% extension ratio, more tensile strength with less elongation at break as the proportion of EAA increase. Aging influence will induce deterioration of mechanical properties, and increase of degree of crystallinity can make the hardness, the modulus at 100% extension ratio and tensile strength increase. The two factors will both have effect on the mechanical properties of EAA/EVA blends. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3110–3117, 2009

**Key words:** damp-heat aging; ethylene copolymer; blend; EVA; EAA

## INTRODUCTION

Ethylene copolymers such as ethylene-vinyl acetate copolymer (EVA), ethylene-acrylic acid copolymer (EAA) have wide range of utilization in different industries.<sup>1</sup> Random incorporation of the vinyl acetate (VA) or acrylic acid (AA) unit into polyethylene progressively hinders the ability of the polymer to crystallize.<sup>1</sup> EVA is a statistically random copolymer, whereas EAA is a more "blocky" random copolymer with AA forming longer "blocks" if sufficient AA is present during polymerization. McEvoy et al.<sup>2</sup> examined the interaction of two types of random copolymers EVA and EAA as compatibilizers with high-density polyethylene, low-density polyethylene, and polypropylene (PP). A polymer blend consisting of nylon 6 and EVA compatibilized with EAA was examined to be toughened and of dramatic increase

in impact strength.<sup>3</sup> As interactions between the two copolymers have scarcely been investigated,<sup>4,5</sup> blends of EAA and EVA is valuable to be studied for their applications.

During long-term use, the ethylene copolymers have to undergo aging or degradation like other polymer materials due to the combined actions of sunlight, heat, moisture, atmospheric oxygen, and so forth. Up to now, many studies focused mainly on either thermal and thermo-oxidative degradation<sup>6–11</sup> or photodegradation.<sup>12–18</sup> Recently, the degradation of ethylene copolymer blends has attracted much attention, for example, EVA blends with different concentration of polyethylene (PE) have been prepared and the heat evolution during two successive heating experiments has been studied by means of differential scanning calorimetry (DSC).<sup>19–22</sup> Our group has investigated the hot air aging of EAA/EVA copolymer blends<sup>23</sup> and damp-heat aging of EVA copolymers with different VA contents<sup>24</sup> in mild aging conditions. Even so, more attention should be paid to the degradation study of ethylene copolymers in mild aging conditions. The objective of this article is to further study the effort of

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relatively mild damp-heat aging on the properties of EVA-EAA blends. Attenuated total reflection (ATR), DSC, wide angle X-ray diffraction (WAXD), and mechanical tests were used for characterization. DSC and WAXD were used to find out the melting and crystallization behavior of the blends in the aging process. ATR was used to characterize the changes of chemical structures, and mechanical tests were performed to study the deterioration of the mechanical properties.

## EXPERIMENTAL

### Materials

EAA (Primacor3002) with AA content percent = 8 wt % and melting flow rate (MFR) = 9.8 g/10min was supplied by Dow Chemical Company (USA). EVA (14-2) was obtained from Beijing Organic Chemical Plant (China) with VA content percent = 14 wt % and MFR = 2.0 g/10 min. They were all supplied in granular forms.

### Preparation method of samples

EAA and EVA blends in various mass proportions of 70/30, 50/50, 30/70, were first mixed and granulated via twin-screw extruder (TE-20, Nanjing Keya Machinery Co., China) with effective length to diameter ratio (L/D) at 32. The extruder had three separate temperature-controlled barrel zones and one die zone, which were set as 120, 140, 150, and 130°C, respectively. Then EAA, EVA, EAA, and EVA blends were injected by small plunger injection molding machine of RR/TSMF type made in United Kingdom by RAY-RAN (POLYTEST) Test Equipment Ltd. The barrel temperature was set as 190°C, whereas the mold temperature was set as 30°C with maximum injection pressure of 110 psi. The mold has a rectangular rut, and the depth was about 2 mm. After laminated, the sheets were cut into dumbbell pieces for tensile testing or retain for infrared spectrometer analysis. In addition, thin films about 0.3 mm of these copolymers blends for measurement of DSC and WAXD were prepared from the injected sheets pressed under 5 MPa between two metal platens at the same temperature of 120°C and cooled between another two metal platens under room temperature.

### Damp-heat aging

Sheet and film samples of EAA/EVA blends prepared above were both placed in a damp-heat testing chamber for aging tests at different intervals of time up to 8 weeks, where the relative humidity was  $93^{+2}_{-3}\%$ , and the temperature was  $40 \pm 2^\circ\text{C}$ . All the

conditions in the damp-heat aging refer to GB/T12000-2003 established in China. Since 40°C was lower than the softening points of these kinds of copolymer blends, the copolymers were solid like rather than melting or transforming during the aging.

### Characterization techniques

ATR-FTIR spectra were achieved by employing spectrometer (Bruker Vector-22) in the range from 580 to 4000  $\text{cm}^{-1}$  with 4  $\text{cm}^{-1}$  resolution.

Thermal analysis was performed on a Perkin-Elmer DSC-7C under an argon atmosphere. The temperature range of scanning was from 0 to 150°C at a heating rate of 10°C/min to observe the endothermic peak of the melting transition. The crystallinity of EAA and EVA blend ( $X_c$ ) was calculated as below:<sup>25,26</sup>

$$X_c = \frac{\Delta H_f}{\Delta H_f^* \cdot c} \times 100\% \quad (1)$$

where  $\Delta H_f^*$  is the enthalpy of fusion of the perfect PE crystal,  $\Delta H_f$  is the enthalpy of fusion of the EAA/EVA blends measured in DSC. The value of  $\Delta H_f^*$  for PE is 277.1 J/g in literature,<sup>27</sup> and  $c$  is the weight ratio of ethylene segments.

To characterize the phases in detail, wide angle X-ray diffraction was done in a Shimadzu XRD-6000 diffractometer (Cu  $K_\alpha$  radiation, 40 kV and 30 mA). The scanning angle  $2\theta$  ranged from 5° to 50° with the scanning velocity of 4°/min. The grain size of crystallite was assigned to be  $L_{hkl}$  which is the lamellar thickness in the direction perpendicular to the (h k l) crystal plane calculated by Scherrer Formula:<sup>28</sup>

$$L_{hkl} = 0.89 \times \lambda / (\beta \times \cos \theta) \quad (2)$$

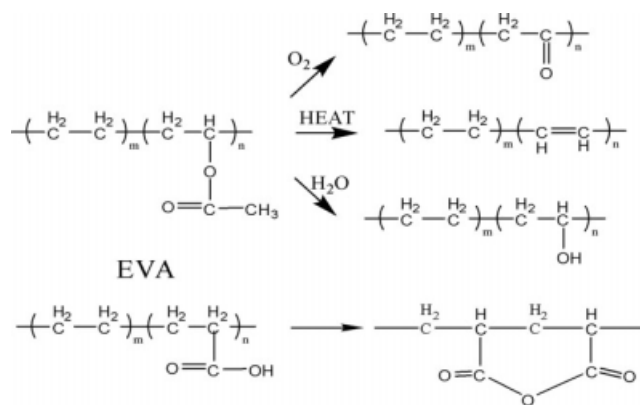
where  $\lambda = 1.54056 \text{ \AA}$  was wavelength of X-ray and  $\beta$  was half-peak width of diffraction peak.

The tensile strength and elongation at break were measured by electronic pulling tester with a cross-head speed of 50 mm/min and a gauge length of 25 mm. The test was conducted under the condition according to ISO 527-1:1993. Shore A hardness of origin and damp-heat aged samples were recorded according to ISO 868:2003.

## RESULTS AND DISCUSSION

### ATR-FTIR characterization of EAA/EVA blends

Scheme 1 presents the degradation mechanism of EVA and EAA due to damp-heat aging. During the damp-heat aging process of EVA and EAA, thermo, oxidation, and damp all have effect on the properties



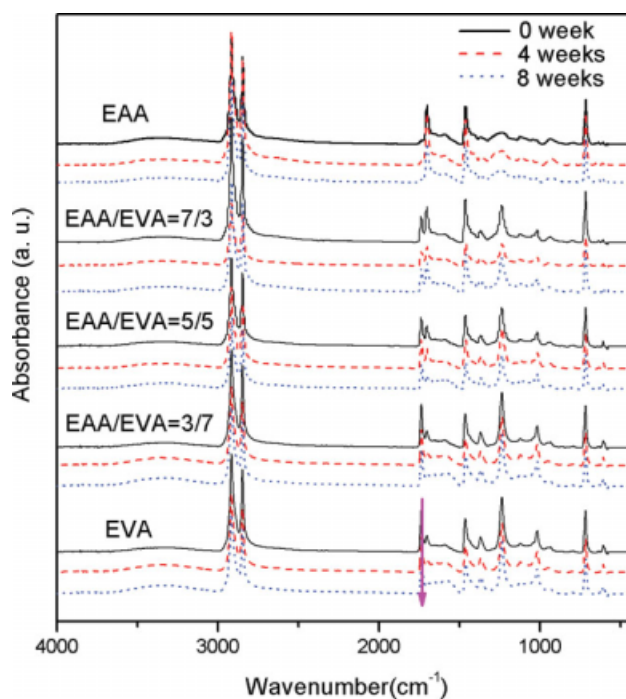
**Scheme 1** Damp-heat aging mechanism of EVA and EAA.

of the copolymers. As reported, EVA copolymers underwent a pyrolysis involving two-step decomposition: an acetate pyrolysis of the copolymer leaving a polyunsaturated linear hydrocarbon and evolving mainly acetic acid, followed by the breakdown of the hydrocarbon backbone to produce a large number of straight-chain hydrocarbon products.<sup>10</sup> Oxidative degradation of EVA copolymers made first the loss of acetoxy groups of the VA units, then degradation of the polymeric chain and finally oxidation of the carbonaceous residue.<sup>29,30</sup> Completely hydrolyzed (EVA) was leading to poly(ethylene-co-vinyl alcohol).<sup>31</sup> For EAA, there were few literatures about the aging of EAA copolymers. In general, the degradation of EAA included first the dehydration to generate poly(circular acid anhydride) and then the decomposition of poly(circular acid anhydride) at higher temperature. However, in this study, the damp-heat aging condition is designed to be mild and will not induce much deterioration. Scheme 1 lists only the first steps of aging consequences. The degradation mechanism is probed by ATR-FTIR.

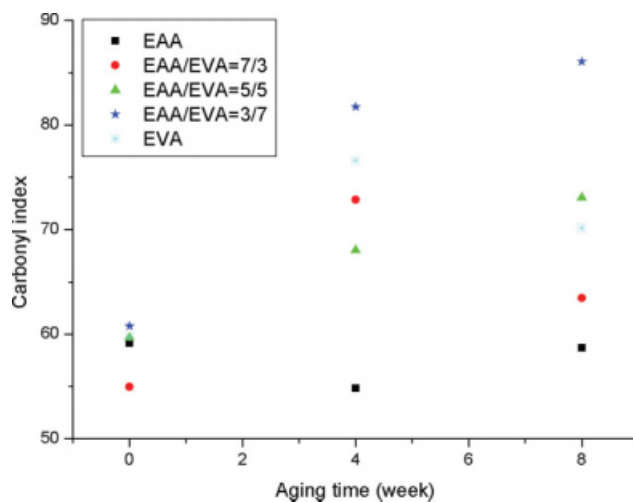
Figure 1 is the ATR-FTIR spectra of EAA, EVA, and their blends before and after several weeks of damp-heat aging (only show results after 4 and 8 weeks aging independently). The characteristic absorption peaks of ethylene segments are as follows: 2920  $\text{cm}^{-1}$  and 2852  $\text{cm}^{-1}$  attributed to the symmetrical and asymmetrical stretching vibration of methylene; 1465  $\text{cm}^{-1}$  attributed to deformation vibration of methylene; 1370  $\text{cm}^{-1}$  attributed to flexural vibration of methyl; 718  $\text{cm}^{-1}$  attributed to inner rocking vibration of methylene.<sup>32</sup> In Figure 1, characteristic absorption peaks of VA groups are as follows: 1740  $\text{cm}^{-1}$  attributed to stretching vibration of C=O band; 1237  $\text{cm}^{-1}$  attributed to asymmetrical stretching vibration of C—O band; 1020  $\text{cm}^{-1}$  attributed to symmetric stretching vibration of C—O—C band.<sup>33</sup> Characteristic absorption peaks of AA

groups is 1702  $\text{cm}^{-1}$  attributed to O=C—O group.<sup>32</sup> Besides the absorption peaks of ethylene segments, peaks at 1702  $\text{cm}^{-1}$  of EAA and 1740  $\text{cm}^{-1}$  of EVA have different strengths due to the different mass ratio of EAA and EVA for various samples of EAA/EVA blends. As aging time increases to 4 weeks or 8 weeks, thermo, oxidation, and damp all have effect on the degradation of the blends. According to Scheme 1, if the damp has effect on the degradation of ethylene copolymers, hydroxyl from VA group will be formed, and peaks around 3300  $\text{cm}^{-1}$  will increase. Obviously in Figure 1, pure EVA presents a visible elevation of peaks around 3300  $\text{cm}^{-1}$  after 8 weeks aging, whereas those of pure EAA has no changes; and as the content of EVA increases, the elevation of peaks around 3300  $\text{cm}^{-1}$  becomes more visible. What's more, thermo and oxidation both make first the loss of acetoxy groups of the VA units and has no influence on the AA units, and then incorporation of oxygen into ethylene segments. So the main sequence of damp-heat aging on the blends is the loss or formation of O=C group.

The course of damp-heat aging is followed by using a carbonyl index (CI) derived from ATR-FTIR measurements.<sup>34</sup> In this study, the CI is defined as the ratio of the peak area between 1850 and 1500  $\text{cm}^{-1}$  ( $A_{1800-1500}$ ) and the absorption peak height at 1463  $\text{cm}^{-1}$  ( $A_{1463}$ ):



**Figure 1** ATR-FTIR spectra of the various EAA/EVA blends before and after several weeks of damp-heat aging. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 2** Carbonyl index variation versus aging time for the various EAA/EVA blends. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

$$CI = A_{1800-1500}/A_{1463}$$

Figure 2 shows the carbonyl index variation versus aging time for the various EVA/EAA blends. Due to the introduction of polar groups, thermal stability of main chain decreases. For EAA with AA content 8 wt %, the CI value has no obvious change, as the mild aging conditions will not have much influence on pure EAA. But for EVA with VA content 14 wt %, the CI value has increased a lot with the aging time, indicating that incorporation of oxygen into ethylene segments happens. CIs of various blends of EAA/EVA all have the same tendency that the CI increases as the aging time increases. This means that in the damp-heat aging process, the main reaction is the incorporation of oxygen into the polymeric chain of EVA in the blends, so that CIs of copolymer blends become larger than that of the no aged samples.

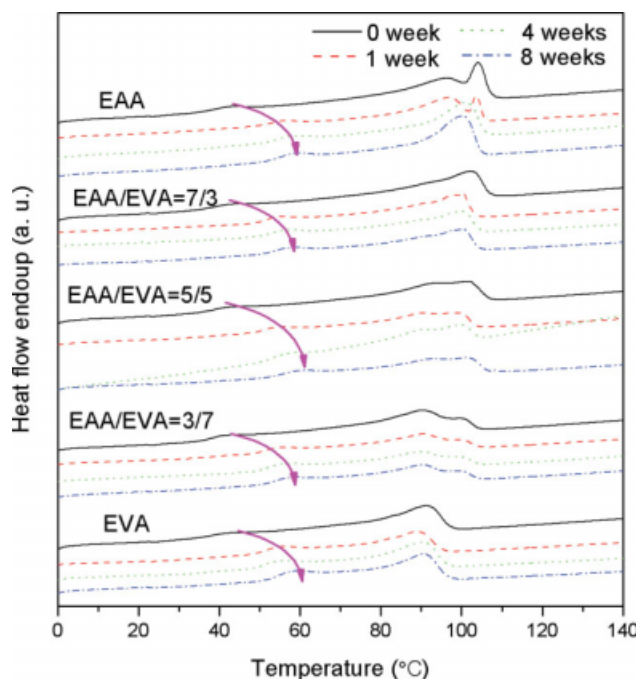
#### Damp-heat aging on crystallization behavior of EAA/EVA blends

It has been reported that the crystallization of ethylene copolymers from the melt state can be described by two stages: primary crystallization and secondary crystallization. During secondary crystallization, it is suggested that the dominant secondary crystallization process is by nucleation on pre-existing crystals, and these secondary crystals are confined to the amorphous regions surrounding the lamellar aggregates.<sup>35</sup>

Figure 3 is the DSC curves of the various EAA/EVA blends before and after several weeks of damp-heat aging. Because of thermal histories, DSC curves

are of multiple peaks which are hard to discuss. We use  $T_{m1}$  for the new formed higher temperature endothermic peak of EAA component after several weeks aging and  $T'_{m1}$  for the new formed higher temperature endothermic peak of EVA after several weeks aging, these peaks or shoulders are attributed to the primary crystallization; because the low temperature crystallization of EVA and EAA blends are miscible, only one  $T_{m2}$  is used to represent the low temperature endothermic peak, which is attributed to the secondary crystallization. The data of melting peaks derived from DSC curves are listed in Table I and degree of crystallinity in Table II in detail.

In Figure 3, the peaks and shoulders at higher temperature are combined to one at 100.5°C for EAA after aging for 4 weeks at 40°C and then has a little increase to be at 101.7°C when aging time is 8 weeks; and for EVA, higher temperature endothermic peaks at 91.3°C are lowered to be at 89.0°C after aging for 1 week at 40°C and then has a little increase to 89.4°C and 89.7°C when aging time is 4 weeks and 8 weeks, independently. For various proportions of EAA and EVA blends, there are multiple endothermic peaks and shoulders, attributed to EAA and EVA independently and the heat enthalpy is proportional to the weight ratio of EAA or EVA.<sup>36</sup> As mentioned, the  $T_{m1}$  and  $T'_{m1}$  are both contributed to primary crystallization which has no time to obtain thermodynamic equilibrium state. After 8 weeks of aging at 40°C, the chains are relaxed in the



**Figure 3** DSC curves of the various EAA/EVA blends before and after several weeks of damp-heat aging. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE I**  
Melting Peaks of Various EAA/EVA Blends as Aging Time Increases

| Samples         | Aging time (week) | $T_{m1}$ (°C) | $T_{m2}$ (°C) | $T_{m1}$ (°C) |
|-----------------|-------------------|---------------|---------------|---------------|
| EAA             | 0                 | –             | 43.7          | –             |
|                 | 1                 | –             | 56.6          | –             |
|                 | 4                 | 100.9         | 58.8          | –             |
|                 | 8                 | 100.2         | 59.5          | –             |
| EAA/EVA = 7/3   | 0                 | 102.3         | 43.7          | –             |
|                 | 1                 | 100.2         | 55.6          | –             |
|                 | 4                 | 99.7          | 57.2          | –             |
|                 | 8                 | 99.7          | 57.9          | –             |
| EAA/EVA = 5/5   | 0                 | 101.9         | 43.7          | 92.6          |
|                 | 1                 | 99.7          | 55.2          | 90.4          |
|                 | 4                 | 100.0         | 57.5          | 90.4          |
|                 | 8                 | 102.1         | 59.9          | 91.1          |
| EAA : EVA = 3/7 | 0                 | 100.2         | 41.9          | 90.2          |
|                 | 1                 | 100.2         | 55.7          | 90.5          |
|                 | 4                 | 99.9          | 56.2          | 90.1          |
|                 | 8                 | 99.9          | 58.0          | 90.2          |
| EVA             | 0                 | –             | 43.1          | 91.3          |
|                 | 1                 | –             | 56.1          | 89.2          |
|                 | 4                 | –             | 55.7          | 90.5          |
|                 | 8                 | –             | 59.0          | 90.5          |

crystal or interphase region, completing the primary crystallization of ethylene copolymers. When the damp-heat aging time at 40°C increases, it can be observed that during 8 weeks of aging,  $T_{m1}$  and  $T'_{m1}$  become close to some content, because the aging process makes the chains with near sequence length reorganize. What's more, when aging at 40°C for some time, reorganization of polymer chains in the interphase or amorphous region happens to form a new ordered domain, which also enhance the degree of crystallinity of various EAA/EVA blends as presented in detail in Table II. Their crystallinity all increase a little when the aging time increases. For pure copolymer, they remain relatively stable as aging time increases from 1 week to 8 weeks. For example, degree of crystallinity of EAA increases from 31.8 to 34.1% when aging time is one week, and remain almost same of 34.5% when aging time is 8 weeks. However, the copolymer blends are all have a less enhance of crystallinity than pure copolymers when aging time increases, probable due to the interaction between EAA and EVA.

The low temperature endothermic peak ( $T_{m2}$ ) of various EAA/EVA blends at about 43.7°C in Figure 3 and Table I are attributed to the secondary crystallization which did not crystallize perfectly. After aging for several weeks at 40°C,  $T_{m2}$  at 43.7°C disappear and new higher temperature peaks appear because of the continuing growth of secondary crystallization due to annealing at 40°C. The melting behavior is consistent with the hypothesis of Marand and coworkers<sup>37</sup> that the slow secondary crystallization at low temperatures leads to crystals with very

poor stability. Besides, we can see that the  $T_{m2}$  is independent of the polar groups' content or variety, just varies as the heating history aging at temperature 40°C. From Gibbs-Thomson equation<sup>38</sup> mean lamellar thickness of low temperature crystallite can be obtained by its melting point through a equation as  $T_m = 414.2(1 - 0.627) \pm 0.8$  K, where  $T_m$  is melting temperature and  $l$  is the lamellar thickness. Remaining possible systematic errors in this equation may involve inhomogeneity of the samples (low molecular weight and copolymer components may reduce the melting temperature due to solvent effects). In our cases, the melting point of low temperature crystallite is increased about 15°C, meaning that lamellar thickness is doubtlessly increased after weeks' aging at 40°C, whatever the ratios of the copolymer blends. It is inferred that the blends of EAA and EVA were miscible throughout the composition range. This is due to the fact that EAA and EVA are polar in nature and are also copolymers of ethylene.<sup>4</sup> Shorter ethylene sequences pinned at lamellar surfaces and are therefore topologically constrained in the crystallization process. As these constraints become more significant, they prevent a number of shorter sequences to take part in further lamellar growth. However, these shorter sequences may be long enough to form stable clusters at sufficiently high undercooling, permitting aggregation between neighboring sequences of the same chain or of other chains.<sup>37</sup> This suggested that the increase of low temperature peaks probably derives from the interphase or even amorphous parts of both EVA and EAA components, in which intermolecular crystallization,<sup>39</sup> or recently said rigid amorphous fraction<sup>40–42</sup> probably occurred.

It has been reported that besides the stable orthorhombic phase (from the primary crystallization), a secondary crystallization phase (monoclinic) also appears in EVA copolymers under normal crystallization conditions (i.e., quenching, aircooling, or solution-crystallized).<sup>43,44</sup> In general, a two-crystal model, say, for example, longer ethylene sequences tend to crystallize into orthorhombic phase and

**TABLE II**  
Degree of Crystallinity of Various EAA/EVA Blends as Aging Time Increases

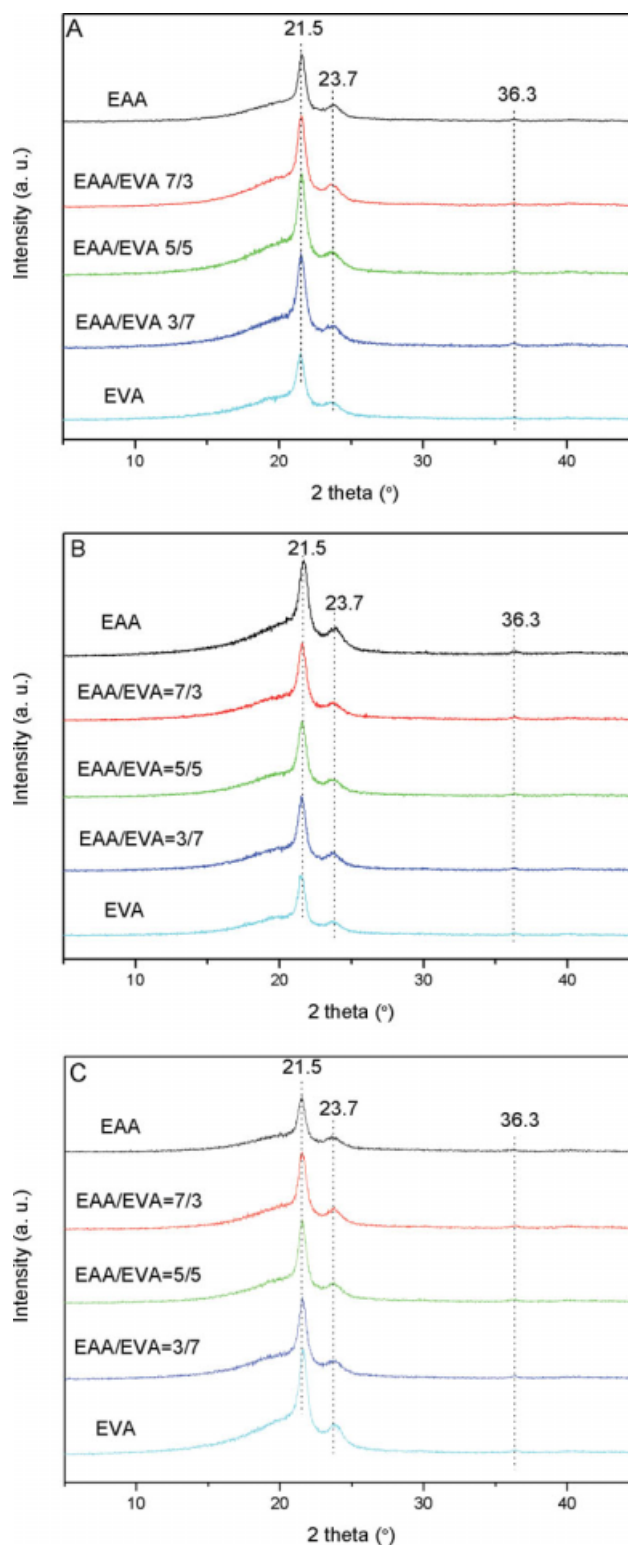
| Samples       | Degree of crystallinity (%) |                    |                    |                    |
|---------------|-----------------------------|--------------------|--------------------|--------------------|
|               | Aging time 0 week           | Aging time 1 weeks | Aging time 4 weeks | Aging time 8 weeks |
| EAA           | 31.8                        | 34.1               | 32.0               | 34.5               |
| EAA/EVA = 7/3 | 30.1                        | 30.5               | 31.8               | 32.0               |
| EAA/EVA = 5/5 | 28.5                        | 31.6               | 31.3               | 30.8               |
| EAA/EVA = 3/7 | 28.9                        | 29.1               | 28.3               | 29.9               |
| EVA           | 25.9                        | 30.5               | 30.7               | 30.9               |

shorter ones tend to crystallize into monoclinic phase, is widely accepted for the long-branch copolymers.<sup>45</sup> Monoclinic phase often exists in the shorter ethylene sequences with more polar groups like VA or AA. Besides the monoclinic, recently the secondary crystallization phase was attributed to third crystalline phase SOCP (possibly hexagonal-like, short time relaxation part of orthorhombic phase) which was detected by solid-state NMR and DSC. Such a third crystalline phase forms during room-temperature aging and melts at the temperature somewhat higher than room temperature on heating.<sup>46</sup>

Figure 4 shows the WAXD patterns of EVA, EAA, and their blends before and after 8 weeks of damp-heat aging. Three perceptible diffractive peaks around 21.5°, 23.7°, and 36.3° are relative to typical (110), (200), and (020) crystallographic planes of orthorhombic phase, respectively. Before [Fig. 4(A)] and after 1 week [Fig. 4(B)] or 8 weeks [Fig. 4(C)] of damp-heat aging, there are not obvious changes in the diffractive peaks. It means that the crystalline phase does not change significantly during the damp-heat aging. The Scherrer equation offers a simple relationship between crystalline size and peak broadening. To give some quantitative comparisons, diffractive parameters of the strongest diffraction peak corresponding to (110) crystallographic plane are listed in Table III. In Table III, before aging, EAA has the largest  $L_{hkl}$  of (110) which is about 110 Å and EVA has the smallest  $L_{hkl}$  (92 Å) among the various copolymer blends. As the EAA content of blends increases, the  $L_{hkl}$  of (110) crystal plane increases because of the longer ethylene chain segments. It is also observed that the  $L_{hkl}$  of (110) crystal plane has the same tendency to increase with the damp-heat aging time. However, the increase of  $L_{hkl}$  of (110) crystal plane are not so much as the increase of degree of crystalline, which indicates the completion of secondary crystallization are able to enhance the degree of crystalline but not the grain size of crystalline.

#### Damp-heat aging on the mechanical properties of EAA/EVA blends

Figure 5 shows the effect of damp-heat aging time on the mechanical properties of the various EAA/EVA blends. The comonomers contents will have a large quantity of effect on the mechanical properties, including hardness, modulus at 100% extension ratio, elongation at break, and tensile strength. As the proportion of EAA increase, the sample has more hardness, more modulus at 100% extension ratio, more tensile strength with less elongation at break. Besides the co-monomers contents, damp-heat aging also has effect on the mechanical properties of



**Figure 4** WAXD patterns of various EAA/EVA blends before (A) and after several weeks of damp-heat aging: B) 1 week C) 8 weeks. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

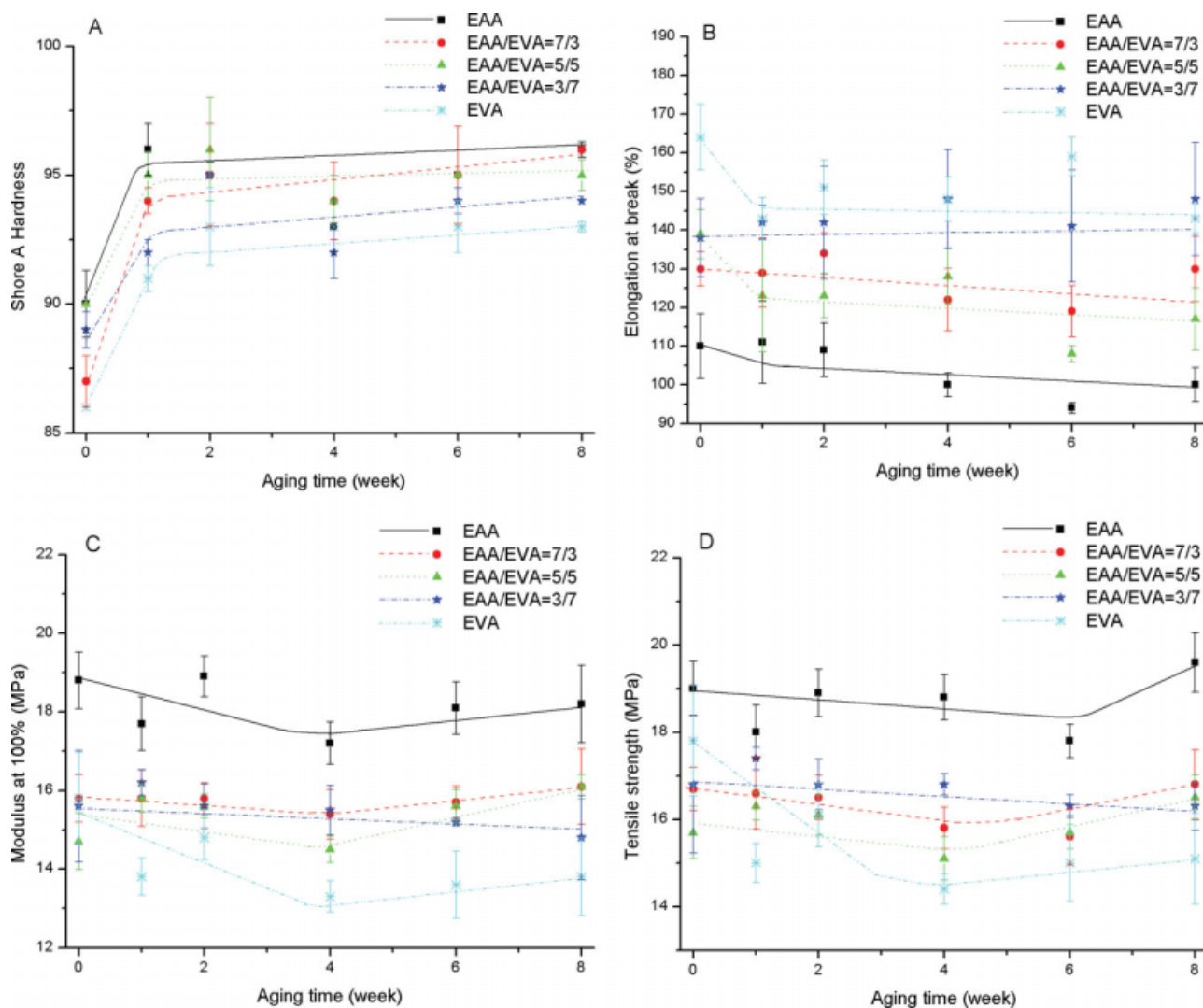
EAA/EVA blends. In Figure 5(A), it is found that the hardness is enhanced a little when the aging time is 1 week, and as the time increases, the

**TABLE III**  
Grain Size  $L_{hkl}$  of (110) Crystal Plane of Various EAA/  
EVA Blends as Aging Time Increases

| Samples       | $L_{hkl}$ (Å) of (110) Crystal plane |                      |                       |
|---------------|--------------------------------------|----------------------|-----------------------|
|               | Aging time<br>0 week                 | Aging time<br>1 week | Aging time<br>8 weeks |
| EAA           | 110                                  | 111                  | 112                   |
| EAA/EVA = 7/3 | 100                                  | 102                  | 105                   |
| EAA/EVA = 5/5 | 98                                   | 98                   | 104                   |
| EAA/EVA = 3/7 | 95                                   | 99                   | 101                   |
| EVA           | 92                                   | 92                   | 94                    |

hardness almost keep stable. This result is accordance to the DSC measurements. Although the primary crystallite did not be influenced so much, the lamellar thickness and degree of crystalline has been improved by damp-heat aging, so that the Shore A

hardness will change a little after 1 week and in the next aging time, due to the stable degree of crystalline, the hardness will not show obvious changes. In Figure 5(B), the elongation at break of EAA and EVA blends is reduced when aging time is 1 week and then keep stable as aging time increases, which probably due to the increase of degree of crystalline. Damp-heat aging also reduces the mechanical properties. In Figure 5(C,D), the modulus at 100% extension ratio and tensile strength both have the same tendency that as the aging time is before 4 weeks, the values are depressed. But as aging time continues to be 8 weeks, the modulus at 100% extension ratio and tensile strength are enhanced again. Figure 5 suggests that aging influence will induce deterioration of mechanical properties, and increase of degree of crystalline can make the hardness, the modulus at 100% extension ratio and tensile strength increase.



**Figure 5** Effect of aging time on the A) Shore A hardness; B) elongation at break; C) modulus at 100% extension ratio; D) tensile strength of the various EAA/EVA blend. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

The two factors will both have effect on the mechanical properties of EAA/EVA blends. However, the existence of EVA will depress the crystallization of EAA, so that EAA/EVA = 3/7 sample shows complicated mechanical behaviors.

## CONCLUSIONS

ATR-FTIR tests show that damp makes the dehydration of EVA which induces the elevation of peaks around 3300  $\text{cm}^{-1}$  after 8 weeks aging. As the content of EVA increases, the elevation of peaks around 3300  $\text{cm}^{-1}$  becomes more visible. Thermo and oxidation both make first the loss of acetoxy groups of the VA units and has no influence on the AA units, so that increase of CIs is owing to the incorporation of oxygen into the polymeric chain of EVA in the blends. By DSC measurements, the low temperature endothermic peak ( $T_{m2}$ ) of various EAA/EVA blends at about 43.7°C attributed to the secondary crystallization is increased with the aging time, which means the lamellar thickness of low temperature crystallite is increased. The increase of low temperature peaks probably derives from the interphase or even amorphous parts of both EVA and EAA components. The crystalline size detected by WAXD and degree of crystallinity have both been improved by damp-heat aging. By mechanical tests, the sample has more hardness, more modulus at 100% extension ratio, more tensile strength with less elongation at break as the proportion of EAA increase. Aging influence will induce deterioration of mechanical properties, and increase of degree of crystallinity can make the hardness, the modulus at 100% extension ratio and tensile strength increase. The two factors will both have effect on the mechanical properties of EAA/EVA blends.

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