

Effects of Compatibilizer on the Layered Silicate/ Ethylene Vinyl Acetate Nanocomposite

Il Soon Suh,¹ Sung Hun Ryu,² Jong Hyun Bae,² Young Wook Chang³

¹Department of Chemical Engineering, Konkuk University, Seoul, Korea

²College of Environment and Applied Chemistry, Kyung Hee University, Yongin-Si, Kyunggi-Do, Korea

³Department of Chemical Engineering, Han Yang University, Ansan, Kyunggi-Do, Korea

Received 22 August 2003; accepted 10 March 2004

DOI 10.1002/app.20962

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Dispersion behavior of monmorillonite (MMT) is investigated in ethylene vinyl acetate (EVA)/MMT nanocomposite with various vinyl acetate content. Maleic anhydride (MAH) grafted polyethylenes with various MAH contents are used as a compatibilizer to enhance the dispersion of MMT. DMA and XRD studies indicate that an intercalated/exfoliated structure is obtained and vinyl acetate content and the concentration of PEMA play a criti-

cal role in EVA/MMT nanocomposite. Higher vinyl acetate content and concentration of grafted maleic anhydride result in better dispersion of MMT. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1057–1061, 2004

Key words: ethylene vinyl acetate; monmorillonite; dispersions; compatibility; nanocomposites; x-ray

INTRODUCTION

Montmorillonite (MMT) is a widely used layered silicate and it consists of layers separated by a van der Waals gap called the gallery or interlayer. These interlayers are occupied by metal cations, which make it difficult to disperse MMT in polymer matrix. Replacing the metal cations with alkylammonium cation is a well known method to improve the dispersion of the MMT in polymer matrix. Various polymer systems are used to form polymer–MMT nanocomposites.^{1,2} Ethylene vinyl acetate copolymer (EVA) is a polyolefin bearing polar vinyl acetate (VA) and it can be synthesized with various VA contents. Alexandre et al.³ showed that sodium–MMT and MMT modified with ammonium cations bearing a carboxylic acid moiety were not suitable for EVA nanocomposite. Zanetti et al.⁴ reported the collapse of the interlayer of octadecylammonium modified MMT in EVA matrix. Improved intercalation behavior was observed with increasing VA content.⁵

The exfoliated and homogeneous dispersion of MMT is reported for a few polymers containing polar groups, such as amide and imide groups.^{6,7} In polypropylene (PP), a typical nonpolar polymer, it is thought that homogeneous dispersion of the silicate layers in PP is difficult due to its nonpolar characteristic. Recently, functional oligomer or comonomer was

used as a compatibilizer to improve the dispersion of silicate layers and maleic anhydride (MAH) grafted polyolefin has been widely used as a compatibilizer.^{5,8–13} Kato et al. used MAH grafted PP (PPMA) oligomer to improve the dispersion of MMT in PP and reported that the number of repeating units per polar group of MAH played a critical role for the exfoliation of MMT in MMT/PP nanocomposite.¹³ Kawasumi et al.⁸ showed that the miscibility between PPMA and PP is more important than the content of grafted MAH content in PPMA to achieve the exfoliation, and better miscibility resulted in improved exfoliation behavior in MMT/PP nanocomposite. Improved dispersity of MMT with increasing amounts of PPMA was also reported.¹⁰ Recently, Zhang et al.¹¹ reported that MAH-grafted PP polymer also enhanced the dispersibility of MMT.

This study investigates the effect of compatibilizer on the intercalation/exfoliation behavior of EVA/MMT nanocomposite. EVA and MMT are melt blended in an internal mixer. Maleated high density polyethylenes (PEMA) with various maleic anhydride contents are used.

EXPERIMENTAL

Materials

EVAs with various vinyl acetate contents were used as matrix polymers. Dimethyl dioctadecyl ammonium-modified montmorillonite (Cloisite[™] 15A) was supplied by Southern Clay Products Inc and it was used as received. 0.5 and 3 wt % maleic anhydride grafted

Correspondence to: S. H. Ryu (shryu@khu.ac.kr).

TABLE I
Characteristics of EVAs Used in this Study

| Symbol | VA content (wt %) | Melt index (g/10 min) | Grade | Producer |
|--------|-------------------|-----------------------|-------|-------------------------------|
| EVA-3 | 3 | 0.6 | EF221 | Hyundai Petrochemical Co. |
| EVA-8 | 8 | 1.0 | EF321 | Hyundai Petrochemical Co. |
| EVA-12 | 12 | 1.1 | EF443 | Hyundai Petrochemical Co. |
| EVA-15 | 15 | 1.6 | E153F | Samsung General Chemicals Co. |
| EVA-22 | 22 | 3.0 | E220F | Samsung General Chemicals Co. |
| EVA-26 | 26 | 4.0 | VS410 | Hyundai Petrochemical Co. |

polyethylene from Aldrich and 1 wt % MAH grafted PEMA (Polybond[™] 3009, MI = 5 g/10 min, Uniroyal) were used as compatibilizer and those were designated as PEMA-05, PEMA-30, and PEMA-10, respectively. Characteristics of EVAs used in this study are shown in Table I.

Nanocomposite preparation

EVA and PEMA were fully melted first and MMT was added using an internal mixer. Melt blend was done at 100°C and concentration of MMT was 5 wt %. Rotor speed was 80 rpm and mixing time was 20 min. The ratio of PEMA was based on EVA/PEMA blend, while MMT concentration was based on EVA or PEMA/EVA blend.

Characterizations

Degree of intercalation/exfoliation was evaluated using X-ray diffractometer (XRD). The thin film of the nanocomposite was prepared by pressing at 100°C. X-ray diffraction patterns of the film of the nanocomposite were obtained by using a M18XHF-SRA diffractometer with CuK α radiation (MacScience Inc). It was scanned from 1.5 to 12° and scanning speed was 2°/min.

Tensile stress at break and tensile modulus were measured using a tensile tester (Tensilon/UTM-III, Toyo-Baldwin) and crosshead speed was 50 mm/min. Test specimens were prepared by pressing at 100°C for 1 min. Ten different specimens were used to obtain the properties and the results were quite reproducible.

The storage modulus of the nanocomposite is determined by using a dynamic mechanical analyzer (DMA 2980, TA Instrument). A sample was subjected to a cyclic strain with an amplitude 0.1% at a frequency 5 Hz. The temperature was increased at a heating rate 2°C/min in the range of -100 to 80°C.

RESULTS AND DISCUSSION

Polar third component has been widely used to improve the dispersion of MMT in polymer/MMT nanocomposites.^{5,8-13} Figure 1 shows the XRD patterns of

EVA-15/MMT nanocomposites with various amount of PEMA-10. The concentration of MMT is 5 wt %. These XRD patterns indicate that interlayers are expanded with increasing amounts of PEMA-10, i.e., intercalation behavior is improved by the addition of PEMA-10, and begin to show mixed random and ordered layer structures at 20 wt % PEMA-10.

The effect of concentration of grafted MAH in PEMA is shown in Figure 2. 20 wt % PEMAs (PEMA-05, 10, and 30) are melt blended with EVA-15. It is observed that intercalation behavior is enhanced with increasing concentrations of grafted MAH. Kawasumi et al.⁸ and Hasegawa et al.¹⁰ also reported that high concentrations of grafted MAH or large amounts of PPMA enhanced the exfoliation of MMT in PP/MMT nanocomposite. Interlayer distances of MMT in EVA-15 nanocomposites with various concentrations of grafted MAH in PEMAs and amounts of PEMAs are shown in Table II. Table II clearly shows that intercalation/exfoliation behavior is dependent on the concentration of grafted MAH and the amount of PEMA. For PEMA-05, interlayer distances of nanocomposites are very similar within the range of 0–20 wt % PEMA, which means that no significant interca-

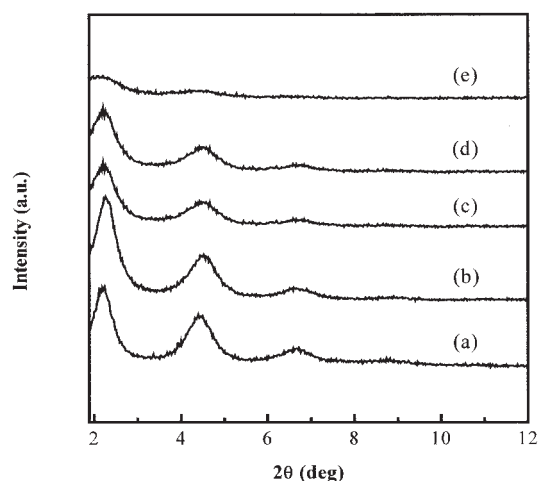


Figure 1 XRD patterns of EVA-15/MMT nanocomposites with various amounts of PEMA-10: (a) 0 wt %; (b) 2 wt %; (c) 5 wt %; (d) 10 wt %; (e) 20 wt %.

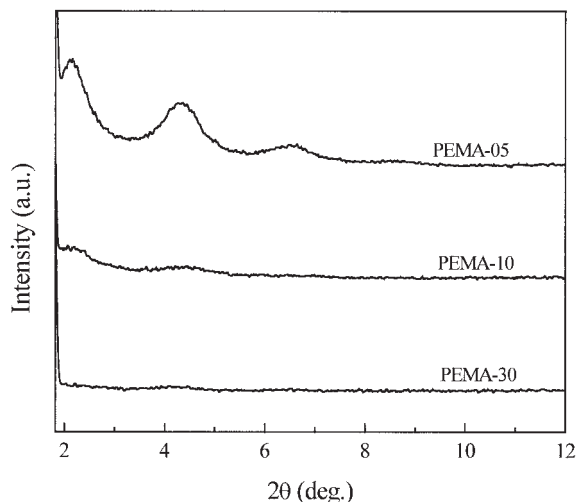


Figure 2 XRD patterns of EVA-15/MMT/PEMA (20 wt %) with various concentrations of grafted MAH.

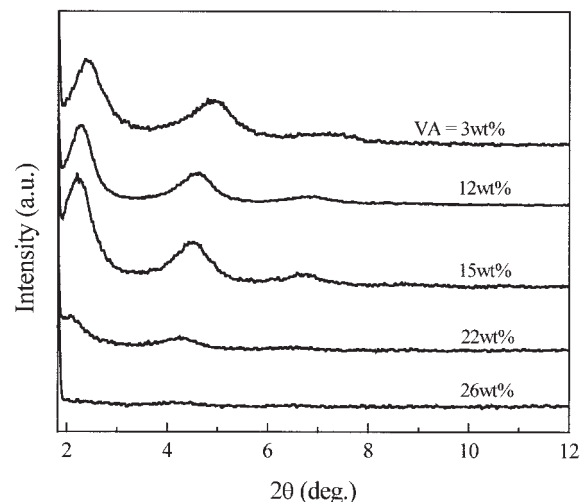


Figure 3 XRD patterns of EVA/MMT/PEMA-10 (10 wt %) with various VA contents.

lation action occurs by the addition of PEMA-05 in this range. It exhibits a relatively broad XRD peak with a shift to the lower angle at 30 wt % and it can be interpreted as the existence of mixed intercalation and exfoliation behaviors. Mixed intercalation/exfoliation and exfoliation are observed at 20 wt % PEMA-10 and PEMA-30, respectively. The amount of PEMA to result in the exfoliation strongly depends on the concentration of MAH in PEMA. Less PEMA is needed for higher concentrations of grafted MAH.

Figure 3 shows the XRD patterns of EVA/MMT/PEMA-10 nanocomposites with various VA content at 10 wt % PEMA-10. It clearly shows that the (001) peak shifts to the lower angle with increasing VA content, which indicates the enhanced intercalation/exfoliation behavior has occurred. However, the effect of VA content on the intercalation/exfoliation in this system is somewhat different from EVA/MMT nanocompos-

ite without PEMA.⁵ Jeon et al.⁵ showed that VA content is an important factor to determine the intercalation/exfoliation behavior in MMT/EVA nanocomposite and critical VA content is 15 wt %. Degree of intercalation/exfoliation increased with VA content up to 15 wt % and it tended to level off at higher VA contents. In Figure 3, however, the (001) XRD peak shifts to the lower angle with increasing VA content even for more than 15 wt % VA content and finally exfoliation behavior is observed for 26 wt % VA content. Different intercalation/exfoliation behaviors between EVA/MMT and EVA/MMT/PEMA-10 nanocomposites under various VA contents clearly come from the addition of PEMA, i.e., the maleic anhydride component of PEMA, and its synergic effect with VA on the dispersity of MMT.

Even though the detailed reasons for the enhanced intercalation behavior by the addition of PEMA at higher VA content and the existence of a critical amount of PEMA to induce the exfoliation as shown in Table II and Figure 3 are not clear yet, two possible explanations exist: different intercalation mechanisms by the addition of PEMA and/or the existence of critical polarity value to cause exfoliation.

For more than 15 wt % VA content, we can assume that the polarity difference between EVA-15 and EVA-26 is not large enough to induce the further change of intercalation, even though the polarity of EVA-26 is higher than EVA-15. This is why interlayer distances of EVA-15/MMT and EVA-26/MMT nanocomposites show similar values⁵ and the existence of critical polarity value for further intercalation can be proposed. The addition of PEMA-10 then results in the increment of polarity of the system and it can exceed a certain critical value to induce further intercalation and exfoliation for high VA content EVAs as shown in

TABLE II
Comparison of Interlayer Distances
of EVA-15/MMT/PEMA

| Material | PEMA content (wt %) | Interlayer distance (Å) |
|----------|---------------------|-------------------------|
| PEMA-05 | 0 | 30.5 |
| | 10 | 30.5 |
| | 20 | 30.8 |
| | 30 | Mixed ^a |
| PEMA-10 | 5 | 30.6 |
| | 10 | 30.8 |
| | 20 | Mixed ^a |
| PEMA-30 | 5 | 30.5 |
| | 10 | 33.1 |
| | 20 | Exfoliated ^b |

^a (001) Peak can not be identified due to broad peak.

^b (001) Peak is not observed.

Figure 3. The presence of critical contents of polar component to achieve a proper exfoliation is also reported for several nanocomposites. Hasegawa et al.¹⁰ and Kato et al.¹³ reported that MAH grafted PP (PPMA) oligomer significantly improved the dispersity of MMT in PP/MMT nanocomposite and critical concentration of MAH is needed to enhance the intercalation behavior. Wang et al.¹² suggested that 0.1 wt % of MAH in PEMA/LLDPE mixture is a critical value for exfoliation for MMT/PEMA/LLDPE nanocomposite.

In addition to the existence of critical polarity, somewhat different intercalation behavior by the addition of PEMA is a possible explanation. In our preliminary experiments, PEMA nanocomposite with 5 wt % MMT showed exfoliation, while EVA (up to 28 wt % VA contents) composites showed intercalation behaviors. This indicates that PEMA has better penetrating ability into the MMT interlayer than EVAs used in our experiments. Some PEMA molecules penetrate into the interlayer prior to EVA molecules in the early mixing step and it weakens the interaction of layers. In this case, the small polarity difference of EVAs can cause the big difference in intercalation capability, because PEMA intercalated layers make easy to penetrate EVA into layers. A similar mechanism is proposed for PP/MMT nanocomposite.¹³ Penetration of PPMA molecules increases the interlayer distance and it makes easy to penetrate PP molecules into layers. Recently it is found that different mixing sequences of materials results in different intercalation behavior in our experiments. Nanocomposite prepared by mixing MMT and PEMA first followed by the addition of EVA shows better intercalation behavior than that prepared by mixing MMT, EVA, and PEMA together. This also may be evidence that penetration of PEMA into MMT layers helps the intercalation of EVA. The

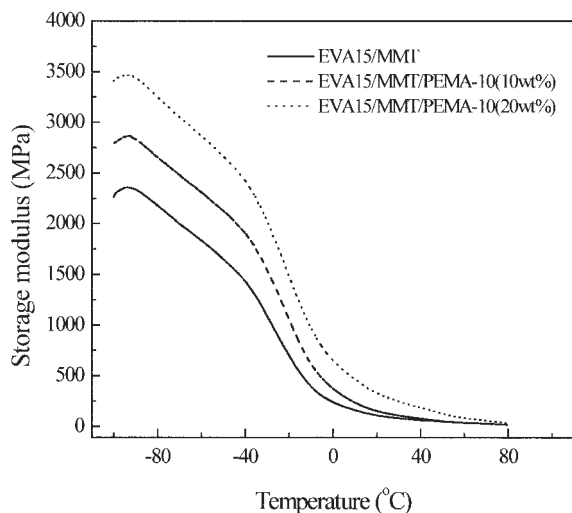


Figure 4 Storage modulus of EVA-15/MMT/PEMA-10.

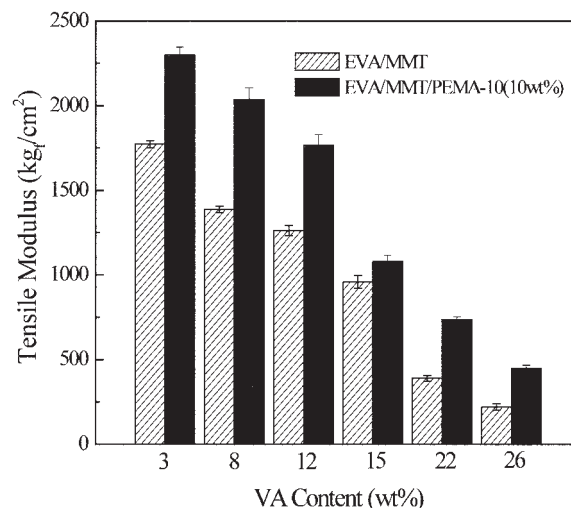


Figure 5 Tensile modulus of EVA/MMT/PEMA-10 (10 wt %) with various VA contents.

roles of EVA and PEMA molecules for the intercalation in EVA/MMT/PEMA nanocomposite are currently under investigation.

Dynamic mechanical tests are carried out to examine the degree of MMT dispersion in EVA-15/MMT/PEMA-10 nanocomposites. Figure 4 shows the effect of PEMA-10 on the storage modulus of nanocomposites as a function of temperature. It is observed that the storage modulus of EVA-15/MMT/PEMA-10 is higher than that of EVA-15/MMT and it increases with the amount of PEMA. The increment of storage modulus is related to the better dispersion of MMT.^{8,13,14} Along with XRD results, DMA results also indicate that the addition of PEMA as a compatibilizer enhances the intercalation of polymer chains into the MMT gallery by the presence of a polar MAH group in PEMA.

Mechanical properties, such as tensile stress and tensile modulus, are characterized using a tensile tester. Figure 5 shows the tensile modulus of nanocomposites as a function of VA content and the addition of PEMA-10. The concentrations of MMT and PEMA-10 are 5 and 10 wt %, respectively. It is observed that tensile modulus increases by the addition of MMT for all VA contents as demonstrated in previous results.^{5,15} The results also show that the addition of PEMA improves the tensile modulus of nanocomposites and it can be attributed to the improvement of MMT dispersion. Hasegawa et al.¹⁰ reported the improvement of the tensile modulus by increasing the amount of PPMA in PP/MMT nanocomposite, which results in greater exfoliation of MMT. Kojima et al.¹⁵ also showed that exfoliated layers of MMT are the main factor for the increment of tensile modulus in Nylon-6/MMT nanocomposite. Tensile stress at break is shown in Figure 6. The

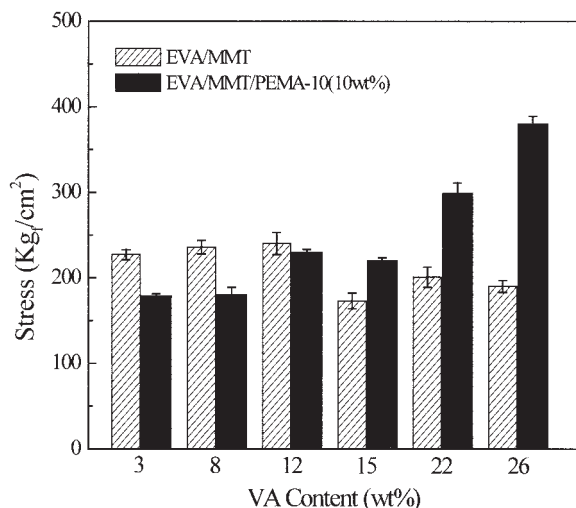


Figure 6 Tensile stress at break of EVA/MMT/PEMA-10 (10 wt %) with various VA contents.

addition of PEMA-10 results in the different trends in tensile stress depending on the VA content. Tensile stress for low VA content EVAs (< 12 wt %) is decreased with PEMA, while it is increased for high VA content EVAs (> 15 wt %). It is also interesting that quite different tensile stress values are observed by the addition of PEMA-10 for nanocomposites with high VA content EVAs, while they show similar tensile stress values without PEMA-10. The addition of 10 wt % PEMA-10 results in 26, 50, and 108% increase of tensile stress for EVA-15, EVA-22, and EVA-26 nanocomposites, respectively. Exfoliated nylon-6 and intercalated PMMA-based nanocomposites exhibit an increase of tensile stress and this behavior is explained by the presence of polar group and even ionic interactions between polymer and silicate layers.¹⁵⁻¹⁷ However, the addition of PPMA to the PP matrix does not induce the increment of tensile stress of PP/MMT nanocomposite and maintains it at an acceptable level. Thus, the significant increase of tensile stress values at higher VA content EVA can be attributed to the high concentration of polar groups in EVA and PEMA.

CONCLUSION

Ethylene vinyl acetate copolymer based monmorillonite nanocomposites are prepared using melt blending. The effects of vinyl acetate content, concentration of grafted maleic anhydride in PEMA, and amount of MMT on the intercalation/exfoliation behavior of MMT are investigated using X-ray diffraction and dynamic mechanical analysis. Dispersibility of MMT is improved with increasing amounts of PEMA and concentration of grafted maleic anhydride in PEMA. The amount of PEMA to accomplish the exfoliation is increased with decreasing concentrations of grafted maleic anhydride. Improvement of dispersibility of MMT under the addition of PEMA is observed with increasing vinyl acetate content and it is attributed to the synergic effect of polar groups, i.e., vinyl acetate and maleic anhydride. DMA results also show that PEMA helps to improve the dispersibility of MMT. The addition of PEMA increases tensile modulus.

References

- Vaia, R. A.; Isii, H.; Giannelis, E. P. *Chem Mater* 1993, 5, 1694.
- Wang, M. S.; Pinnavaia, T. J. *Chem Mater* 1994, 6, 468.
- Alexandre, M.; Beyer, G.; Henrist, C.; Cloots, R.; Rulmont, A.; Jerome, R.; Dubois, P. *Macromol Rapid Commun* 2001, 22, 643.
- Zanetti, M.; Camino, G.; Thomann, R.; Mulhaupt, R. *Polymer* 2001, 42, 4501.
- Jeon, C. H.; Ryu, S. H.; Chang, Y. W. *Polym Int* 2003, 52, 153.
- Usuki, A.; Kawasumi, Y.; Kojima, M.; Fukushima, Y.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1179.
- Yano, K.; Usuki, A.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Part A: Polym Chem* 1993, 31, 2493.
- Kawasumi, M.; Hasegawa, N.; Kato, M.; Usuki, A.; Okada, A. *Macromolecules* 1997, 30, 6333.
- Yoon, J. T.; Jo, W. H.; Lee, M. S.; Ko, M. B. *Polymer* 2001, 42, 329.
- Hasegawa, N.; Kawasumi, M.; Kato, M.; Usuki, A.; Okada, A. *J Appl Polym Sci* 1998, 67, 87.
- Zhang, Q.; Fu, Q.; Jiang, L.; Lei, Y. *Polym Int* 2000, 49, 1561.
- Wang, K. H.; Choi, M. H.; Koo, C. M.; Choi, Y. S.; Chung, I. J. *Polymer* 2001, 42, 9819.
- Kato, M.; Usuki, A.; Okada, A. *J Appl Polym Sci* 1997, 66, 1781.
- Alexander, M.; Dubois, P. *Mater Sci Eng* 2000, 28, 1.
- Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Part A: Polym Chem* 1993, 31, 1755.
- Lee, D. C.; Jang, L. W. *J Appl Polym Sci* 1996, 61, 1117.
- Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Part A: Polym Chem* 1993, 31, 983.