

HIGHLIGHT

Review of Melt-Processed Nanocomposites Based on EVOH/Organoclay

N. ARTZI,¹ M. NARKIS,¹ A. SIEGMANN²

¹Department of Chemical Engineering, Technion—Israel Institute of Technology, Haifa 32000, Israel

²Department of Materials Engineering, Technion—Israel Institute of Technology, Haifa 32000, Israel

Received 3 August 2004; revised 1 February 2005; accepted 16 March 2005

DOI: 10.1002/polb.20481

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

ABSTRACT: EVOH nanocomposites containing organically treated clays are unique systems in which the clay is strongly attracted to EVOH, thus affecting the morphology and the resultant thermal and mechanical properties. A strong effect of the processing conditions on morphology, thermal, and mechanical properties was observed. In highly interacting systems, under dynamic mixing conditions, in addition to a fracturing process of the clay particles, an onion-like delamination process is suggested. EVA-g-MA

and LLDPE-g-MA, having polar groups, were studied as compatibilizers to further induce clay intercalation and exfoliation. The compatibilizers affected both the thermal and mechanical properties of the composites at different levels. Thermal analysis showed that with increasing compatibilizer content lower crystallinity levels result, until at a certain content no crystallization has taken place. A Ny-6 (nylon-6)/EVOH blend is an interesting host matrix for incorporation of low organoclay contents. The

Ny-6/EVOH blend is a unique system that tends to hydrogen bond and also to *in situ* chemically react during melt mixing. The addition of clay seems to interrupt the chemical reaction between the two host polymers at certain compositions, leading to lower melt blending torque levels when clay is present. A competition between Ny-6 and EVOH regarding the intercalation process takes place. However, Ny-6 seems to lead to exfoliated structures, whereas EVOH forms intercalated structures, as revealed

Correspondence to: M. Narkis (E-mail: narkis@tx.technion.ac.il)

Journal of Polymer Science: Part B: Polymer Physics, Vol. 43, 1931–1943 (2005)
© 2005 Wiley Periodicals, Inc.

from combined XRD and TEM experiments, owing to thermodynamic considerations and preferential localization of the clay in Ny-6. Of special interest is the increased

storage modulus seen by the presence of only 1 wt % clay, which was achieved by extrusion under high shear forces, leading to a completely exfoliated structure. ©2005

Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 43: 1931–1943, 2005

Keywords: melt-processed nanocomposites; EVOH/organoclay



NATALIE ARTZI

Dr. Natalie Artzi received her B.Sc. (1977) in Chemical Engineering at the Technion – Israel Institute of Technology. After serving as an officer in the army, she joined that department again for a direct path towards Ph.D. with Professor Moshe Narkis. Her research focused on nanocomposite systems containing clay. Currently, she is a postdoctorate fellow in the department of Chemistry at the Massachusetts Institute of Technology with Prof. JoAnne Stubbe, studying non-template driven polymerization reactions and the use of bioengineering methods to generate new biodegradable polymers.



MOSHE NARKIS

Moshe Narkis is Professor of Chemical Engineering at the Technion – Israel Institute of Technology. He has published 300 scientific articles and graduated 70 M.Sc. and Ph.D. students. He is a 2003 Fellow of PMSE-ACS, recipient of the 2002 Paul J. Flory Polymer Research Prize, and the 2001 SPE Research Award. He was President of the Israel Polymer and Plastics Society and elected Honorary Member of the Society. He was Editor-in-Chief of two journals and currently member of the Advisory Board of several journals, including Polymer Engineering and Science, Polymer Composites, and Polymers for Advanced Technologies.



ARNON SIEGMANN

Professor Arnon Siegmann received his B.Sc. (1964) and M.Sc. (1966) in Chemical Engineering at the Technion – Israel Institute of Technology and his Ph.D. (1969) in Macromolecular Science, with Professor P.H. Geil, at Case Western Reserve University, Cleveland, OH. After several years of industrial research, he joined the Department of Materials Engineering at the Technion (1978) where he has served on its faculty ever since. His main interests include immiscible polymer blends, particulate polymer composites, conductive plastics and processing, structure, property relationships.

INTRODUCTION

The expansion of industrial and economic activities results in a continuous need for new materials of improved performance. The demand of lightweight high-performance materials in the past 30 years is so great and diverse that the composite materials concept is a natural outcome. The main difference between nanocomposites and conventional composites is that in the former the filler has at least one dimension in the nanometer range.^{1,2} Polymers filled with low amounts of layered silicate dispersed on the nanoscale level are promising materials characterized by a combination of chemical, physical, and mechanical properties that cannot be obtained by dispersion of inorganic fillers in the micron level.³

Ethylene vinyl alcohol copolymer (EVOH) is a thermoplastic resin related to polyvinyl alcohol (PVOH) with improved extrudability and water resistance while maintaining most of PVOH's advantages; gas barrier, oil resistance, and transparency. EVOH is produced by complete hydrolysis of vinyl acetate groups present in the random copolymer. A high degree of hydrolysis is required (over 99wt %).⁴

A particular EVOH composition range is required to achieve good barrier properties, that is, 25–45 mol % ethylene content. If the ethylene content is more than 50 mol %, EVOH is not a high barrier resin, owing to characteristic higher oxygen transmission coefficient values. On the other hand, EVOH is hygroscopic, and thus for practical applications, reduction of oxygen barrier properties owing to moisture absorption cannot be neglected. A wide variety of polymers can be employed in a filmed multilayer structure along with EVOH. Such multilayered structure should conform to EVOH under various processing conditions such as blow molding, thermoforming, and orientation.⁵

EVOH offers innovative food-packaging technology owing to reduced oxygen permeability. An outstanding characteristic of EVOH is its high level of hydrogen bonding and the retention of crystallinity in all copolymer compositions, despite the irregularity and nonstereospecificity of the vinyl alcohol segments distributed in the EVOH copolymer chain. This behavior is a result of dense chain packing of the copolymer components, because only small spatial interruptions in EVOH occur owing to the relatively small volume of the hydroxyl groups. Therefore, the randomness of the hydroxyl groups does not have a significant effect on crystallinity reduction as in other random copolymers.

Mechanical properties of EVOH depend on the ethylene content. Increasing the ethylene

content from 25 to 45 mol % leads to strength and modulus decrease. Elongation increases and impact strength decreases with increase of ethylene content. Presumably, with variation of the ethylene content, the cohesive intermolecular hydrogen bonds and crystallinity are changed, thus affecting chain flexibility.⁴

Coleman⁶ studied the miscibility of EVOH with EVA and polymethacrylates. He found that miscible EVOH blends with polymers containing ester or acetoxy groups do exist. Another research⁷ has shown partial miscibility in blends of two random copolymers: EVOH and copolyamide. The rich EVOH blends exhibited much lower miscibility levels than those of the copolyamide-rich blends; the latter even showed interpolymer complexes in the amorphous phase through hydrogen bonding. The ethylene content in EVOH affected the miscibility of the blends where a higher ethylene content resulted in a lower miscibility. This was attributed to reduced hydrogen bonding between OH groups of EVOH and amide groups of the copolyamide. EVOH copolymers have the potential of forming partially miscible blends in the amorphous phase with a wide variety of polymers containing polar functional groups, due to the significant role of the hydrogen bonding interaction.

Although nanocomposites based on organoclays and homopolymers have been extensively investigated, nanocomposites based on organoclays and polymer blends are relatively rare. Interesting materials that combine the properties of polymer blends and the nanometric clay can be achieved. Ellis⁸ investigated the barrier properties of clay nanocomposites based on PA6 and EVOH as a matrix. A reference nanocomposite containing PA6 and 4 wt % clay was found to offer 10-fold reduction in the diffusion coefficient of methanol compared to neat PA6. Nanocomposites containing PA6 and EVOH were found to produce miscible blends that maintained complete clay exfoliation up to 50 wt % EVOH. At higher levels (75 wt %) of EVOH content, the clay became ineffective as a barrier and the permeability was severely reduced. The latter phenomenon was found to be caused by clay aggregates.

This study summarizes the behavior of polymeric organoclay composites emphasizing relationships of morphology with the related thermal and mechanical properties, considering material properties and processing parameters. Commercial organoclays were used in combination with EVOH as the matrix with and without compatibilizers (EVA-*g*-MA, or LLDPE-*g*-MA). Also, a Nylon-6/EVOH blend was reinforced with organoclays and its behavior studied.

MATERIALS

The EVOH (ethylene vinyl alcohol copolymer) used in this study is a commercial product, Kuraray, Japan, consisting of 32 mol % ethylene. Several treated clays were used: Nanomer-I.30E (E-clay), an onium ion modified montmorillonite mineral. The organoclay used contains 70–75 wt % montmorillonite and 25–30 wt % octadecylamine. It is claimed to be designed for ease of dispersion into amine-cured epoxy resins to form nanocomposites. Nanomer-I.35L (L-clay), a modified montmorillonite mineral containing 60–70 wt % montmorillonite and 30–40 wt % polyoxyethylene decyloxypropylamine claimed to be treated for EVOH resins. Nanomer-1.30TC, which is claimed to be designed for ease of dispersion into Ny-6 to form nanocomposites. A reference untreated clay was also used. All clays were obtained from Nanocor (Illinois).

PREPARATION METHODS

Composites were prepared by a standard procedure of melt mixing of a dry-blended mixture of the components in a Brabender Plastograph machine equipped with a 50 cm³ cell, at 230 °C and 60 rpm (or 250 °C and 20 rpm when Ny-6 was also incorporated) for approximately 45 min. The melt-mixing step was performed also in a Haake Rheocord 90 mixer (Haake GmbH, Germany) at 230 °C, at 60 and 150 rpm. The resulting composites were subsequently compression molded at the same temperature at 1000 MPa to produce 3 mm-thick plaques.

Composites were also prepared by extrusion in an intermeshing twin-screw, Brabender TSC 42/6 (L/D = 6; D = 42 mm), at 200 and 220 °C, using two screw rotation speeds (20 and 40 rpm). Filaments of the blends produced were ground and injection molded using an Arburg 220/150 injection-molding machine, equipped with an ASTM standard mold. The injection molding machine temperature was maintained at 200 or 220 °C in all zones, and the mold at 40 °C. Selected composites were compression molded after compounding (rather than injection molded) at the extrusion temperature (i.e., 200 or 220 °C), under a pressure of 1000 MPa, into 3 mm-thick plaques.

CHARACTERIZATION

Differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), dynamic mechanical

thermal analysis system (DMTA, Perkin Elmer Series 7), X-ray diffractometer (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), and FT-Raman spectra were employed for characterization as reported elsewhere.^{9–14} The nonextractable EVOH content was also determined using several solvents.¹²

RESULTS AND DISCUSSION

EVOH/Clay System

Intercalation and/or delamination of organoclay in the presence of EVOH (ethylene vinyl alcohol copolymer), can be accomplished by melt mixing in a Brabender Plastograph. Figure 1 shows the mixing torque as a function of mixing time for a 85/15 EVOH/clay blend, for two types of clay, that is, organically treated (I.30E) and untreated as a reference material. Under the dynamic melt mixing conditions, the gradual viscosity increase reflects on the fracturing of the organoclay particles into smaller aggregates and also between lamina, followed by a delamination process, eventually leading to the dispersion of thin clay platelets in the EVOH matrix. Thus, under dynamic conditions delamination, in addition to intercalation, may be a major step. Under static “blending” conditions, that is, prolonged heating without shearing, intercalation is the dominant step.^{15–17} Figure 1 shows that the mixing torque, or viscosity, of the composite with the untreated clay is

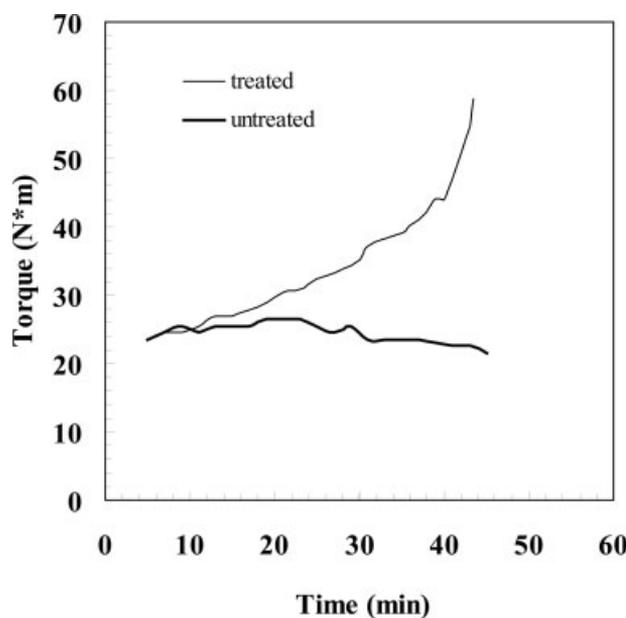


Figure 1. Brabender plastograms of 85/15 EVOH/clay blends at 230 °C and 60 rpm.⁹

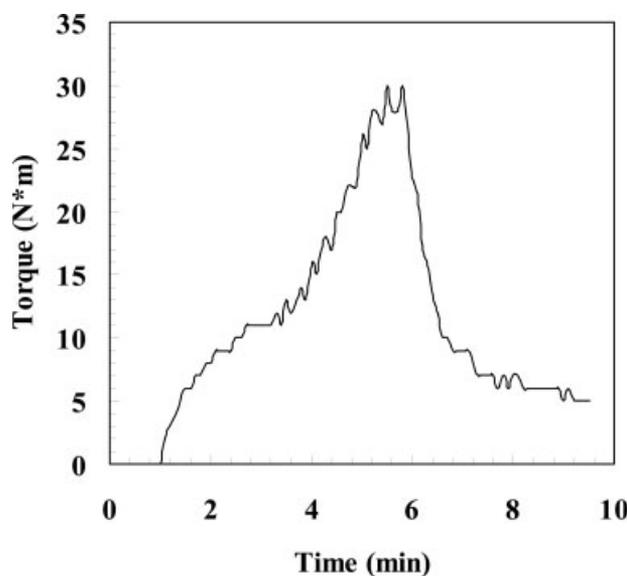


Figure 2. Haake plastogram of an 85/15 EVOH/treated clay blend at 230 °C and 150 rpm.⁹

almost constant, implying that the clay particles stay practically intact, thus behaving as regular filler particles. However, the viscosity of the system with treated clay rises due to the fracturing processes, formation of new surfaces, and increased interaction with the EVOH matrix. Filler agglomeration/deagglomeration processes may also play a role on the level of the required mixing power (torque), where the matrix character and interaction level are important parameters.¹⁸ The effect of the combination of high temperature and high rotation speed (150 rpm compared to 60 rpm), experienced in a Haake machine, is demonstrated in Figure 2. An interpretation of this behavior is that when the separately dispersed platelets reach a certain concentration, presumably when platelets continuity is approached and a gel-like behavior becomes important, a dramatic viscosity increase occurs. The temperature, set at 230 °C, has actually reached 280 °C near the maximum torque level seen in Figure 2. The torque rise became pronounced already after 3 min of mixing, presumably at the beginning of formation of platelets continuity, and the maximum torque level occurred soon thereafter at 5.5 min. The material's rigidity is increasing due to the increasing level of EVOH/clay interaction, thus eliminating segments and chains from the flowing polymer melt. The sharp torque decrease (Fig. 2) is a result of mechanical degradation of the hot "gelled" mass under the dynamic mixing conditions, which occurs when the system

flowability decreases, attaining a certain low level. At this point the material is undergoing milling into powder, in the hot mixing cell. In highly interacting systems, in addition to a fracturing process of the clay particles, an onion-like delamination process is suggested, as schematically illustrated in Figure 3. External tactoid platelets are subjected to dynamic high shear forces, which ultimately cause peeling off and their delamination from the stack of layers building the original clay particle.⁹

DSC studies offer further support to the high interaction level in the EVOH/clay system. Second DSC runs of the neat EVOH that was melt mixed for 45 min, and for the 85/15 EVOH/treated clay blend at two mixing times, 10 and 45 min, was done (not shown here). The composite that was melt mixed for 10 min shows a T_m of 178.9 °C, similar to the neat EVOH (179.6 °C), but a lower enthalpy value, 72.2 mJ/g (normalized to EVOH content), compared to 82.7 mJ/g for the neat EVOH. After 45 min of mixing much lower melting temperature and enthalpy values, 159.5 °C and 55.5 mJ/g, respectively, are found. Segmental chains attached to the platelets are partially hindered from taking part in the flow process and their crystallization process is also hindered. Thus, the platelets affecting the crystallization process are both the EVOH intercalated clay particles and those platelets that are already dispersed. These results differ from reports on other systems, where the clay was acting as a nucleating agent.^{15,16,19-21} The EVOH crystallization process is quite sensitive to crystallization conditions. The crystallization process in the presence of clay particles, especially clay nanoplatelets, generates "smaller" EVOH crystals, having a lower melting temperature. The clay is probably playing a role of hindering the crystallization process, owing to the high interaction level with EVOH.⁹

EVOH/Compatibilizer/Clay Systems

In an attempt to further improve the interaction level between the EVOH matrix and the clay tactoids, thus increasing the levels of intercalation and exfoliation, different compatibilizers were studied including maleic anhydride-grafted EVA (EVA-*g*-MA), or maleic anhydride-grafted LLDPE (LLDPE-*g*-MA). Figure 4 shows the mixing torque as a function of mixing time for the systems containing EVA-*g*-MA as a compatibilizer. The plastograms shown are affected by the EVA-*g*-MA content and even show an abrupt tor-

que upturn. The viscosity of EVA-g-MA containing 15 wt % clay is low and slightly decreases with time. When 1 wt % EVA-g-MA is added to

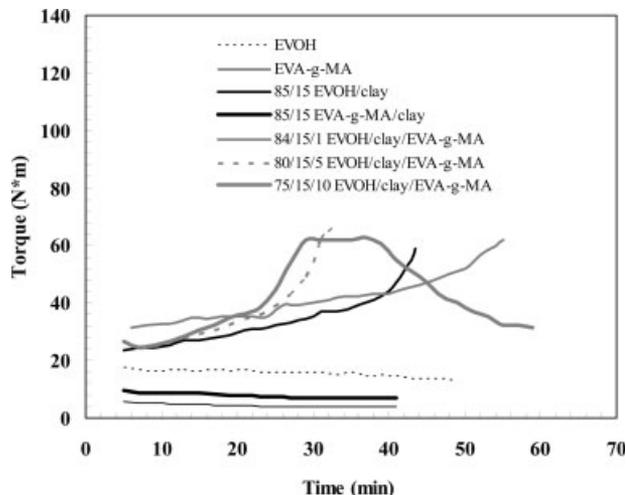
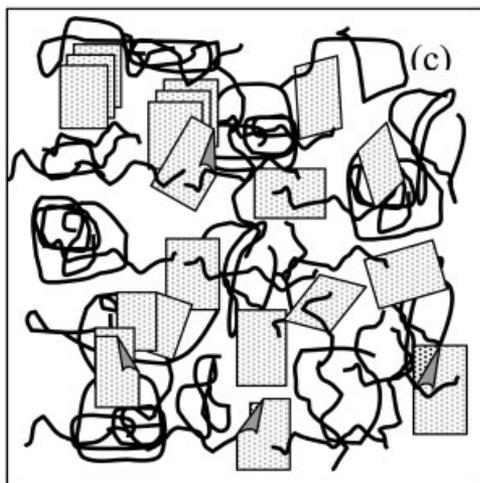
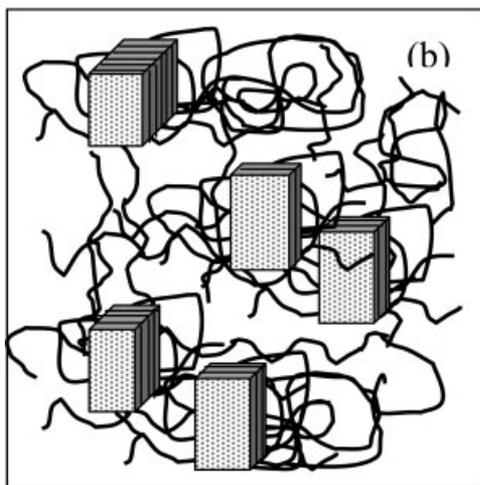
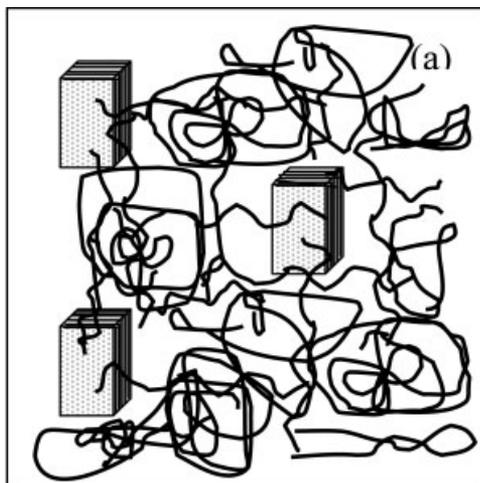


Figure 4. Brabender plastograms of EVOH/clay systems containing EVA-g-MA, at 230 °C and 60 rpm.¹¹

EVOH containing 15 wt % clay, the torque rise is delayed compared to the reference 85/15 EVOH/clay system. However, using 5 and 10 wt % EVA-g-MA shortens the time for the torque to rise by 15 and 18 min, respectively. The neat EVOH, neat EVA-g-MA and blends containing the same amounts of EVA-g-MA (without clay, not shown here) show a stable constant torque as a function of mixing time. Although the EVA-g-MA viscosity is much lower than that of neat EVOH, EVOH containing 1 wt % EVA-g-MA has a higher viscosity than the neat EVOH. For higher EVA-g-MA contents, the torque level decreases. The sharp torque decrease seen after 40 min of mixing when 10 wt % compatibilizer was incorporated, in the presence of 15 wt % clay, is a result of mechanical grinding into powder of the hot mass under the dynamic mixing conditions. Although LLDPE-g-MA viscosity is similar to that of neat EVOH, higher than that of EVA-g-MA, the blends containing the same amounts of compatibilizers exhibited lower torque values when LLDPE-g-MA was used. The Brabender results (Fig. 4) showing the gradual viscosity increase, which is more pronounced in the presence of the compatibilizers, is indicative of more fracturing of the organoclay particles.

Figure 3. Schematic description of clay fracturing and an onion-like delamination process, where thin platelets peel off and disperse in the matrix:⁹ (a) before interclation and/or delamination process; (b) interclation and clay fracturing; and (c) advanced delamination process.

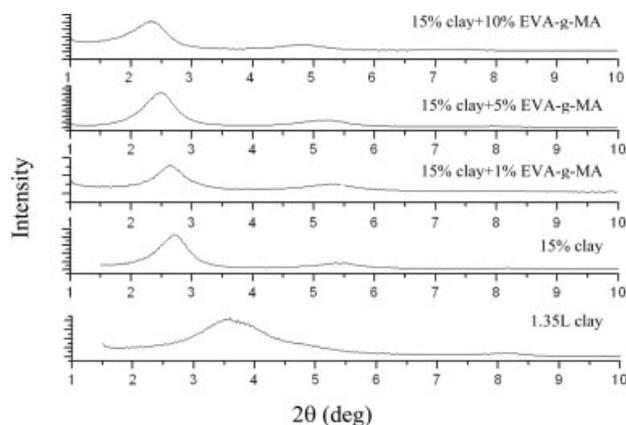


Figure 5. X-ray diffraction patterns of EVOH/clay systems containing EVA-g-MA.¹¹

The clay fractures into small aggregates and also undergoes delamination processes. The improved interaction level between the EVOH and the clay, when compatibilizers are added, leads to significant viscosity rise and shorter times of torque upturn are realized.

X-ray diffraction is a conventional method to characterize the gallery height in clay particles, which is indicative of the extent of intercalation. Figure 5 shows the X-ray diffraction patterns of neat clay, [85/15 EVOH/clay], and blends containing EVA-g-MA as compatibilizers. The increase in the clay basal spacing in the presence of EVOH is higher for the compatibilized systems, and is more significant for the larger compatibilizer amounts. The neat clay shows a characteristic peak at $2\theta = 3.58^\circ$ ($d_{001} = 25 \text{ \AA}$). The blending of 15 wt % clay with EVOH has resulted in an intercalated structure with a gallery spacing of 32 \AA ($2\theta = 2.72^\circ$). Reference samples of 85/15 EVA-g-MA/clay and 85/15 LLDPE-g-MA/clay were examined to characterize the tendency of each compatibilizer by itself to intercalate, showing significantly different gallery heights of 42 and 29 \AA , respectively. The EVOH/clay systems containing 1, 5, and 10 wt % EVA-g-MA exhibit characteristic peaks at 2.6, 2.5, and 2.3° ($d_{001} = 33, 35, \text{ and } 38 \text{ \AA}$), respectively. The gallery heights of the corresponding blends containing LLDPE-g-MA are 34, 35, and 38 \AA , respectively, the same as obtained for the EVA-g-MA. Although EVA-g-MA itself tends to intercalate more than LLDPE-g-MA and more than EVOH, the final gallery heights were similar for the two compatibilizers. When EVA-g-MA is added there may be a competition between the compatibilizer and the EVOH molecules regard-

ing the intercalation process. Therefore, in this case, probably EVA-g-MA is also intercalated and more EVOH remains outside the galleries compared to the external content of EVOH when LLDPE-g-MA is used.

Although no changes in thermal properties of EVOH in EVOH/compatibilizer systems were seen, significant changes have occurred when both clay and compatibilizer were incorporated. Surprisingly, when 1wt % of either compatibilizer was used, the interruption to the crystallization process was less pronounced than without the compatibilizer, that is, the EVOH/clay system (Table 1). In the case where 1wt % EVA-g-MA was added, the EVOH crystallinity was slightly higher than that without this compatibilizer. However, when increasing amounts of compatibilizers of either type are used, the interruption to the EVOH crystallization process is more pronounced until at a certain concentration no crystallization occurs. This stems from the high interaction levels developed between the EVOH and the clay in the presence of the compatibilizers; thus, ultimately, EVOH segments cannot crystallize. EVOH chains attached to platelets are partially hindered from participating in the flow process and crystallization. Moreover, the intercalation level increases for higher compatibilizer contents; therefore, more delamination and exfoliation occur, resulting in more single platelets dispersion, which further

Table 1. Torque Data in Extrusion of EVOH/clay Composites

Composite	Torque (N*m)
200 °C, 20 rpm	
Neat EVOH	45–50
EVOH+1%1.35L, 1st pass	105–115
EVOH+1%1.35L, 2nd pass	150–190
EVOH+1%1.35L, 3rd pass	110–150
200 °C, 40 rpm	
Neat EVOH	50
EVOH+0.5%1.35L, 1st pass	90–110
EVOH+0.5%1.35L, 2nd pass	110–130
EVOH+0.5%1.35L, 3rd pass	130–150
EVOH+1%1.35L, 1st pass	270
EVOH+1%1.35L, 2nd pass	70
EVOH+1%1.35L, 3rd pass	80
220 °C, 40 rpm	
Neat EVOH	20
EVOH+1%1.35L, 1st pass	23
EVOH+1%1.35L, 2nd pass	23
EVOH+1%1.35L, 3rd pass	30

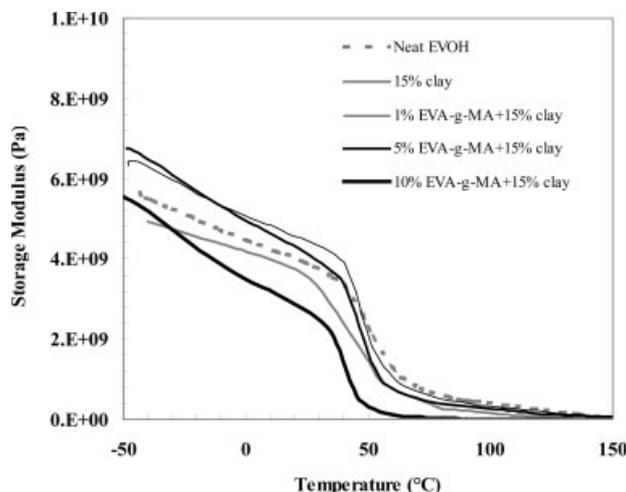


Figure 6. Storage modulus of EVOH/clay systems containing EVA-g-MA.¹¹

reduces crystallization, and more EVOH chains are confined in the galleries.

The different interaction levels of the compatibilizers with EVOH and the resulting fracturing levels of the clay affect the storage moduli of the blends. The fracturing/delamination processes result in two opposing effects on the storage modulus. The first, common in nanocomposites, increases the modulus due to the increased level of polymer/clay interaction. The second, unique to the presently studied EVOH matrix, results in a modulus decrease due to the dramatic degree of crystallinity drop, ultimately even to its elimination. It is concluded, based on the comprehensive thermal analysis studied, that the degree of crystallinity is playing a major role in the mechanical behavior of the presently studied EVOH nanocomposite systems.

LLDPE-g-MA is more effective than EVA-g-MA in the reduction of the degree of crystallinity in the EVOH/clay composites. Hence, LLDPE-g-MA monotonically decreases the storage modulus by increasing its content (Fig. 6). Differently, EVA-g-MA initially increases the modulus and subsequently at higher contents decreases the modulus (Fig. 7).¹² The difference between the two compatibilizers in their effect on crystallinity and the derived mechanical properties is not obvious. It is suggested that LLDPE-g-MA presence leaves more crystallinity depressing "bare" clay surfaces than the EVA-g-MA. This is due to the latter being a better intercalant, and the former therefore being at a higher content in the matrix, external to the clay particles. Because LLDPE-g-MA interaction with clay is lower than

EVA-g-MA's, more bare clay surfaces are available for interaction with EVOH. This clay/EVOH interaction is the one responsible for the reduction in the degree of crystallinity, as shown in Table 1.

Ny-6/EVOH/Clay

Nanocomposites based on organoclays dispersed in immiscible polymer blends, namely Nylon-6 (Ny-6)/EVOH/clay, were also studied. Diagrams of mixing torque versus time at 250 °C for neat Ny-6 and neat EVOH, and their 50/50 blends with and without clay are presented in Figure 8. The EVOH torque decreases with time owing to a gradual thermal degradation at the 250 °C processing temperature, becoming practically constant after 30 min of mixing. The Ny-6 torque level is constant with mixing time. As for the 50/50 Ny-6/EVOH blend, the torque levels are higher than those of each of the neat constituent polymers, and in fact, significantly increase with mixing time. Literature reports on EVOH/nylon blends processed in an extruder, characterized by low residence times (several min), describe the formation of intermolecular hydrogen bonds between the amide and hydroxyl groups of Ny-6 and EVOH, respectively.^{22,23} Indeed, at the short mixing times, formation of hydrogen bonds may be dominating; however, for the longer mixing times (up to 45 min), another mechanism seems to dominate, leading to the significantly increasing torque level seen already after about 20 min of mixing. It is

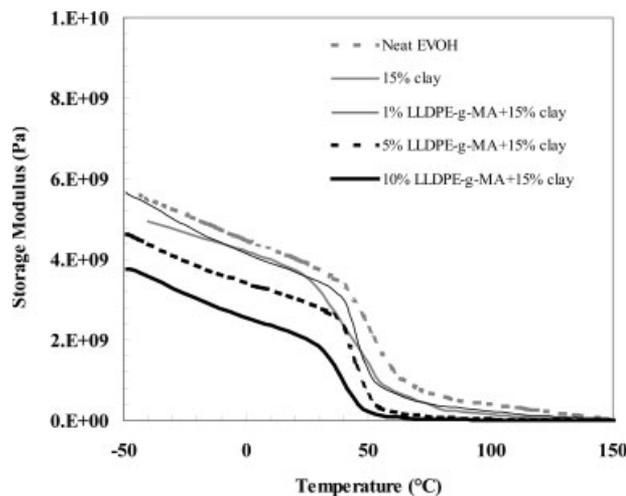


Figure 7. Storage modulus of EVOH/clay systems containing LLDPE-g-MA.¹¹

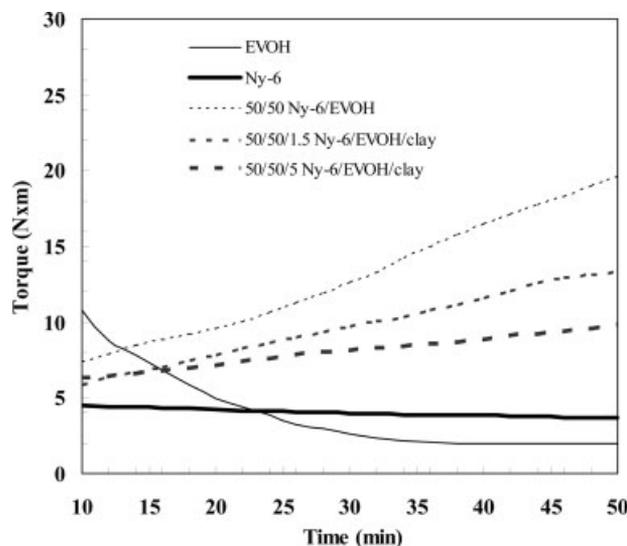


Figure 8. Brabender plastograms of neat EVOH, Ny-6, 50/50 Ny-6/EVOH, 50/50/1.5 and 50/50/5 Ny-6/EVOH/clay, at 250 °C and 20 rpm.¹⁴

important to note that although neat EVOH undergoes reduction in melt viscosity, that is, scission reactions, the torque of the 50/50 Ny-6/EVOH blend significantly increases. Hence, a chemical reaction between the polar groups of the constituent polymers may be taking place, in addition to the formation of hydrogen bonds, as was recently suggested.⁹ Most likely at 250 °C chemical reactions have taken place between EVOH hydroxyl groups and carboxyl terminal groups of Ny-6. Surprisingly, the addition of clay to the 50/50 Ny-6/EVOH blend results in lower torque levels, becoming more pronounced for the higher clay content (Fig. 8), although the torque still increases with mixing time. The latter behavior may be interpreted by considering the competition between several mechanisms, that is, intercalation, exfoliation, preferential localization of the clay in one of the polymers and, as suggested, occurrence of chemical reactions. Owing to the intercalation processes, which occur already after short mixing times, less EVOH and Ny-6 chains are available outside the clay galleries for chemical reactions to take place, thus leading to the lower torque levels (viscosity), compared with the torque levels of the blend without clay, that is, 50/50 Ny-6/EVOH blend (Fig. 8). Although after longer mixing times fracturing processes and delamination are taking place (verified by XRD and TEM), leading to new availability of the neat polymers outside the galleries, there might not be suffi-

cient time for them to chemically react during melt mixing. Moreover, based on XRD and TEM results, it seems that a larger clay fraction is intercalated and surrounded by Ny-6 rather than by EVOH; hence, the torque increase is expected to be less significant, as seen in Figure 9 for the neat polymers in the presence of the clay.

As clay is added to the 50/50 Ny-6/EVOH blend a competition between EVOH and Ny-6 regarding intercalation is taking place. When 1.5 wt % clay is added to the blend a complete exfoliated structure is obtained. However, when 5 wt % clay is added to the blend there is a shoulder-like peak at $2\theta = 1.8^\circ$, similar to the location of the peak seen when 5 wt % clay is added to neat EVOH. The peak is, however, broader and lower in intensity suggesting more exfoliated fraction compared to the case of only EVOH with 5 wt % clay (Fig. 10). This is also verified by TEM (Figs. 11 and 12) and implies that in the 50/50/5 Ny-6/EVOH/clay system, more Ny-6 chains are intercalated compared with the amount of intercalated EVOH chains. The clay is thus preferentially located within the Ny-6 phase. This is also supported by the result that addition of clay to the 75/25 Ny-6/EVOH blend, where Ny-6 is the major component, leads to an exfoliated structure irrespective of clay content, that is, 1.5 or 5 wt % (lack of basal reflections, Fig. 10). Hence, the lower

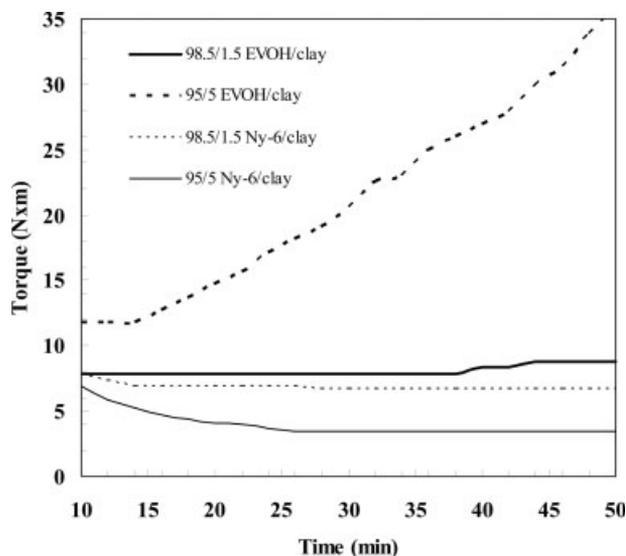


Figure 9. Brabender plastograms of near 98.5/1.5 and 95/5 Ny-6/clay and 98.5/1.5 and 95/5 EVOH/clay, at 250 °C and 20 rpm.¹⁴

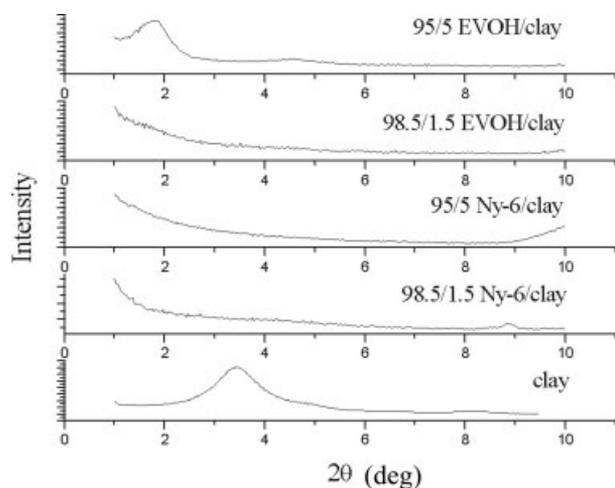


Figure 10. X-ray diffraction patterns of neat clay, 98.5/1.5 and 95/5 Ny-6/clay and 98.5/1.5 and 95/5 EVOH/clay Brabender cell mixing, at 250 °C for 50 min.¹⁴

the EVOH content in the blend is, the higher the delamination level achieved. This is in agreement with Ellis's study⁸ on PA-6/EVOH nanocomposites, who found that increasing the content of EVOH in the blend (75 compared to 50 wt %) induces intercalation instead of exfoliation owing to thermodynamic considerations.

Extrusion Processing of EVOH/Clay Systems

EVOH nanocomposites containing low clay concentrations processed by twin-screw extrusion compounding were studied. In highly interacting systems containing a polar matrix, such as EVOH, the maximum clay content that can be incorporated may be operationally limited. In the present study, using the Brabender machine's counter rotating intermeshing twin-screw extruder, a

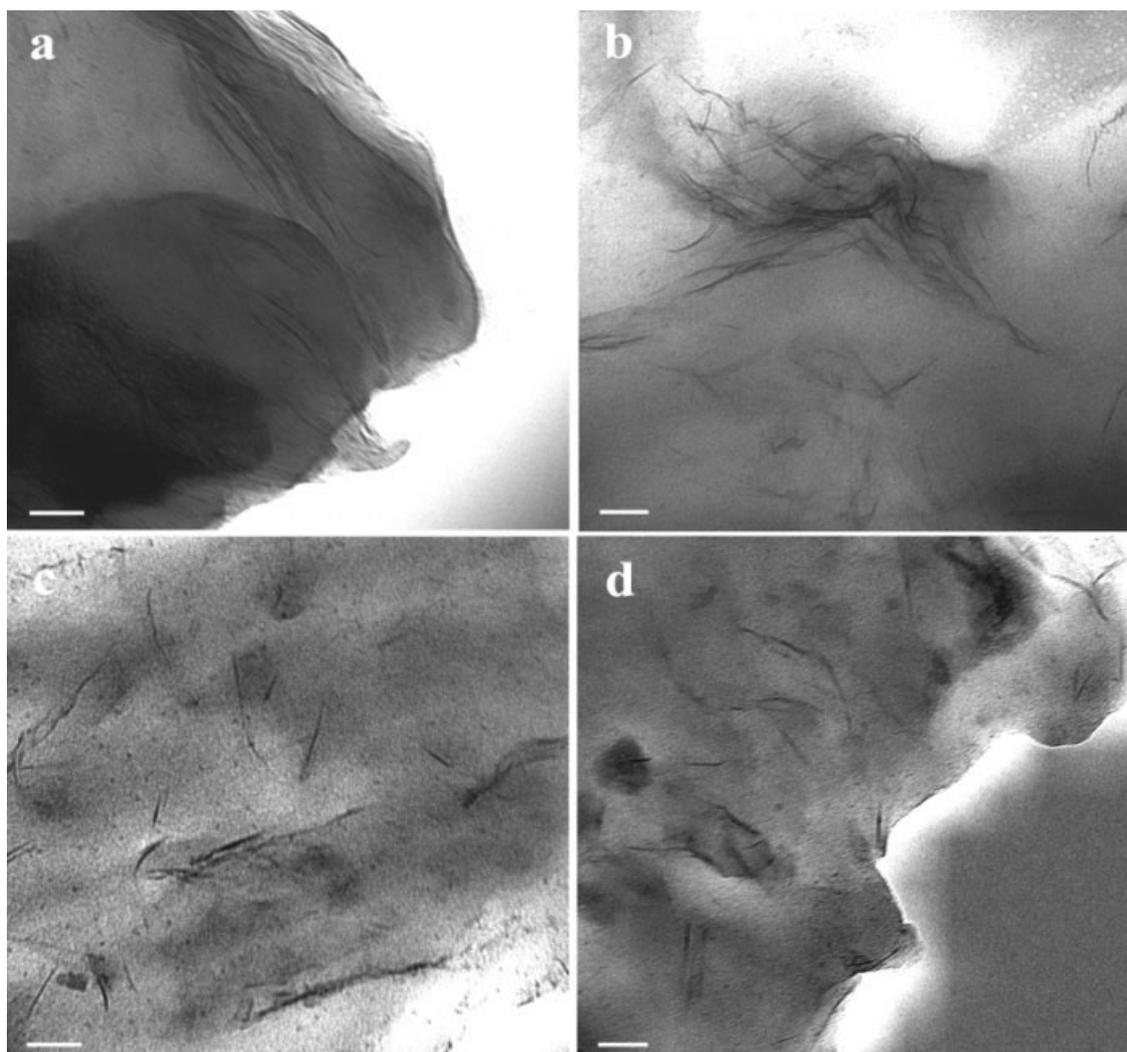


Figure 11. TEM micrographs of 50/50/5 Ny-6/EVOH/clay Brabender cell mixing, at 250 °C for 50 min (bar = 50 nm).¹⁴

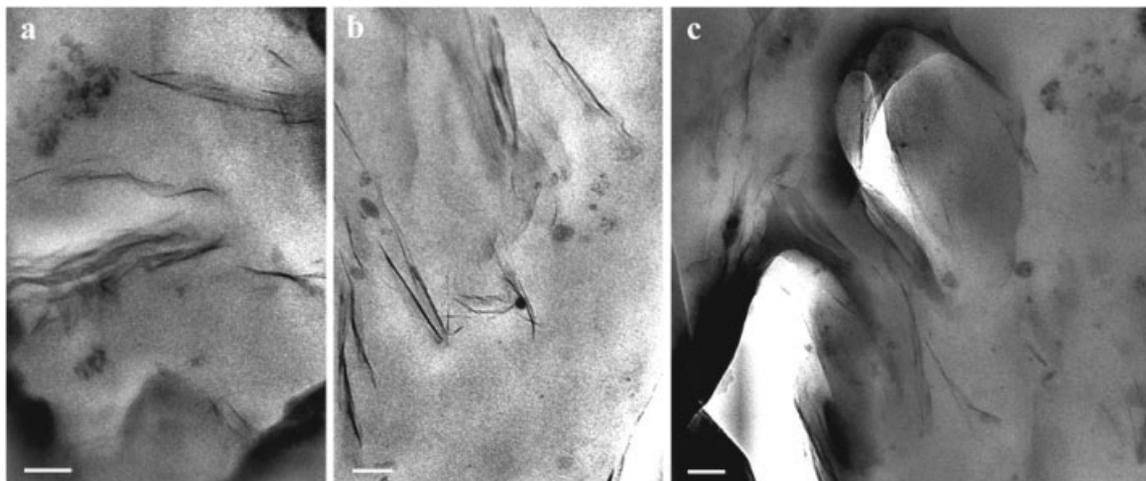


Figure 12. TEM micrographs of 50/50/1.5 Ny-6/EVOH/clay Brabender cell mixing at 250 °C for 50 min (bar = nm).¹⁴

high torque level was developed, which enabled the use of up to 1 wt % clay. To explore the effect of the processing residence time on the composite properties, materials were reinserted into the extruder for three successive passes. Already after the first extrusion pass, the torque was very high (Table 2), indicating that clay particles were fractured and exfoliated.

The XRD diffraction pattern of composites processed at 200 °C and 20 rpm exhibited no clay reflections already after the first extrusion pass (not shown here). The composite processed at 200 °C and 40 rpm had an exfoliated structure (no characteristic basal reflection peak); however, the low reflection intensity after the first pass further decreases by the additional extrusion passes (Fig. 13). Because at 40 rpm the residence time is half that of at 20 rpm, the longer residence times in the former (second and third passes) result in higher delamination and platelets dispersion. Another factor contri-

buted to the higher delamination level is the higher stress developed at the elevated rotational speed. Figure 14 shows a representative TEM micrograph for EVOH containing 1 wt % clay processed at 200 °C and 40 rpm, after the first extrusion pass. Delaminated platelets marked by arrows are embedded in the EVOH matrix. Figure 14(a) and (b) represent different regions in the sample. More regions were observed (not shown here), showing the same morphology, in agreement with the X-ray diffraction results.

Extrusion residence time, three successive extrusion passes, screw rotational speed, and the processing temperature were all found to affect the morphology and the associated thermal and mechanical properties.¹³ For the composites processed at 200 °C, regardless of clay type or content, the tensile modulus and strength substantially increased relative to the neat EVOH, without impairing the Izod impact resistance. The

Table 2. Thermal Characteristics of EVOH/Clay/Compatibilizer Nanocomposite Systems Containing EVOH and 15 wt % Clay

	T_c (°C)	ΔH_c (mW/g)	T_m (°C)	ΔH_m (mW/g)
EVOH	160	60	180	82
EVOH+15%clay	341	29	156	32
1% EVA- <i>g</i> -MA	158	35	166	41
5% EVA- <i>g</i> -MA	132	30	159	34
10% EVA- <i>g</i> -MA	—	0	—	0
1% LLDPE- <i>g</i> -MA	157	30	162	35
5% LLDPE- <i>g</i> -MA	98	15	135	20
10% LLDPE- <i>g</i> -MA	—	0	—	0

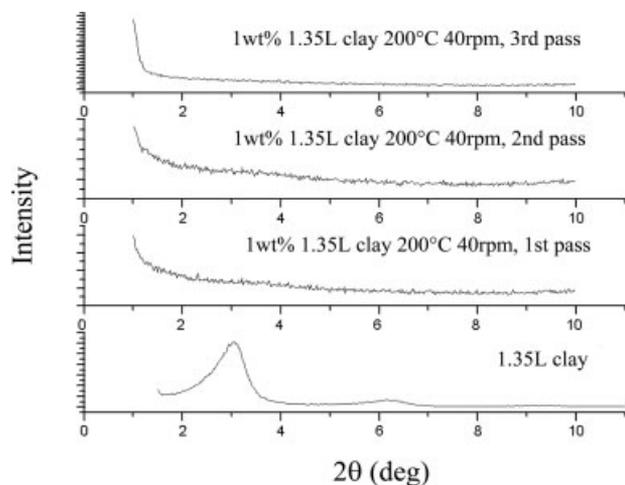


Figure 13. X-ray diffraction patterns of 99/1 EVOH/1.35L clay composite after first, second, and third extrusion passes at 200 °C and 40 rpm, and injection molding at 200 °C.¹⁴

modulus and yield strength increase upon the addition of only 0.5 wt % organoclay by 40 and 30%, respectively. Such significant improvements for this low clay content, are achieved by

the exfoliated clay platelets without an opposing effect of EVOH crystallinity drop at this very low clay content.

CONCLUSIONS

1. EVOH is a unique polymeric matrix in organoclay–nanocomposites owing to the strong EVOH/clay interaction level developed.
2. The general accepted notion that intercalation is a preceding step to exfoliation is not necessarily valid in the melt-processed EVOH-based systems, where the dynamic high shear forces may lead to peeling off individual platelets.
3. Dynamic melt mixing of EVOH/organoclay mixtures is accompanied by high mixing torque levels owing to clay particle fracturing, intercalation, and delamination processes and the buildup of significant levels of polymer/clay interaction, thus requiring only low clay contents for properties modification.

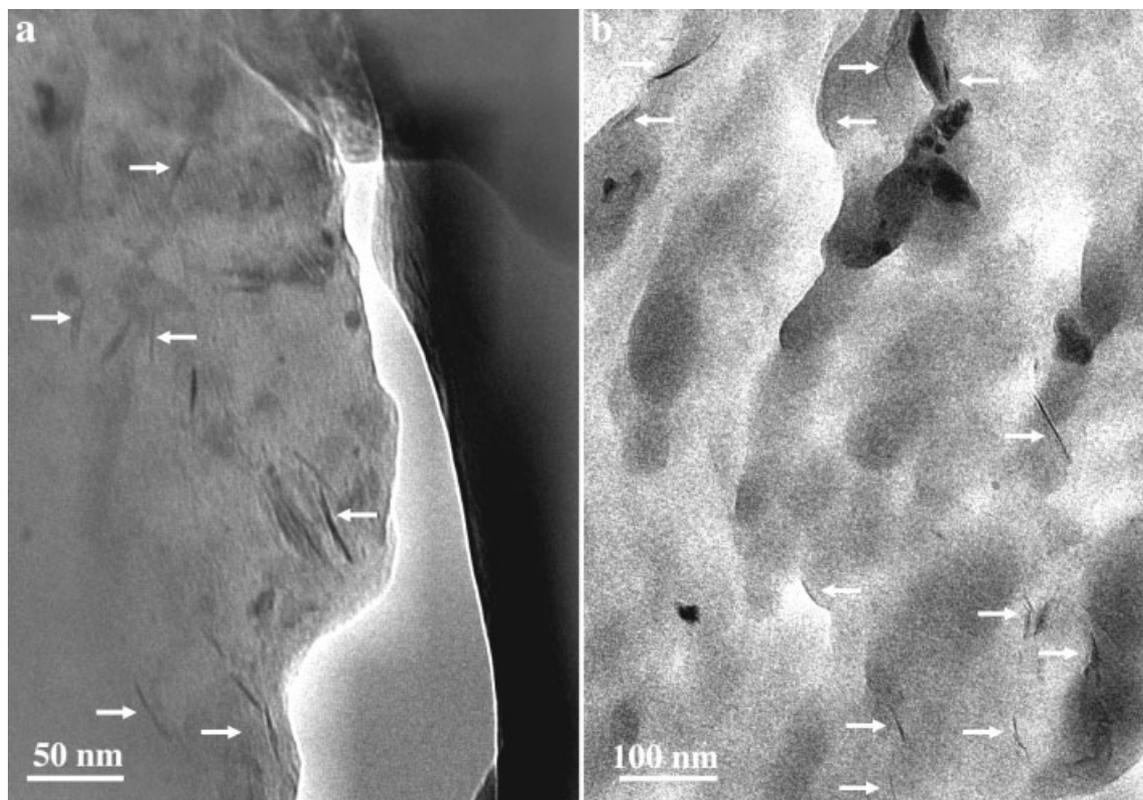


Figure 14. TEM micrographs of 99/1 EVOH/clay composite after first extrusion pass at 200 °C and 40 rpm, and injection molding at 200 °C.¹⁴

4. Mixed clay morphology of intercalation and delamination, or complete exfoliation can be achieved, depending on blending conditions.
5. Competition between the clay platelets reinforcing effect and degree of crystallinity depression determine the final physical and mechanical behavior of the nanocomposites.
6. When incorporating clay into a multicomponent system, considerations such as the nature of the blend components and their physical properties, the blend composition, clay content, and extent of interaction of the components are significant parameters in determining the clay particles location, and the structure and resultant properties of the systems.
7. From a practical point of view EVOH/clay nanocomposites may be engineered and their properties tailored, according to processing conditions.

REFERENCES AND NOTES

1. Lee, A.; Lichtenhan, J. D. *J Appl Polym Sci* 1999, 73, 1993.
2. Reichert, P.; Kressler, J.; Thomann, R.; Mulhaupt, R.; Stoppelmann, G. *Acta Polym* 1998, 49, 116.
3. Zanetti, M.; Lomakin, S.; Camino, G. *Macromol Mater Eng* 2000, 279, 1.
4. Iwanami, T.; Hirai, Y. *TAPPI J* 1983, 66, 85.
5. Ikari, K. *New EVOH Development*; Kuraray: Japan, 1986.
6. Coleman, M. M.; Yang, X.; Zhang, H.; Painter, P. C. *J Macromol Sci Phys* 1993, B32, 295.
7. Nir, Y. PhD Thesis, Department of Chemical Engineering, Technion, Israel Institute of Technology, Haifa, 1996.
8. Ellis, T. S. *Polymer* 2003, 44, 6443.
9. Artzi, N.; Nir, Y.; Wang, D.; Narkis, M.; Siegmann, A. *Polym Comp* 2001, 22, 710.
10. Artzi, N.; Nir, Y.; Narkis, M.; Siegmann, A. *J Polym Sci Part B: Polym Phys* 2002, 40, 1741.
11. Artzi, N.; Nir, Y.; Wang, D.; Narkis, M.; Siegmann, A. *Polym Comp*, 2001, 24, 627.
12. Artzi, N.; Khatua, B. B.; Tchoudakov, R.; Narkis, M.; Brener, M.; Siegmann, A.; Lagaron, J. M. *J Macromol Sci Part B: Physics* 2004, B43, 605.
13. Artzi, N.; Tzur, A.; Narkis, M.; Siegmann, A. *Polym Comp* 2005, 26, 343.
14. Artzi, N.; Khatua, B. B.; Narkis, M.; Siegmann, A. *Polym Comp*, submitted.
15. Giannelis, E. P. *Adv Mater* 1996, 8, 29.
16. Liu, Z. Qi; Zhu, X. *J Appl Polym Sci* 1999, 71, 1133.
17. Kornmann, L. A.; Berglund, J. Sterte; Giannelis, E. P. *Polym Eng Sci* 1998, 38, 1351.
18. Bhagawan, S. S.; Tripathy, D. K.; De, S. K. *J Appl Polym Sci* 1987, 34, 1581.
19. Vaia, R. A.; Vasudevan, S.; Krawiec, W.; Scanlon, L. G.; Giannelis, E. P. *Adv Mater* 1995, 7, 154.
20. Ratto, J. A.; Steeves, D. M.; Welsh, E. A.; Powell, B. E. *Southern Clay, ANTEC* 1999; p. 1628.
21. Lee, D. C.; Jang, L. W. *J Appl Polym Sci* 1996, 61, 1117.
22. Nir, Y.; Narkis, M.; Siegmann, A. *Polym Eng Sci* 1998, 38, 1890.
23. Incarnato, L.; Acierno, D.; Ruso, P.; Malinconico, M.; Laurienzo, P. *J Polym Sci. Part B: Polym Phys* 1999, 37, 2445.