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# Effects of Modified MMT on Mechanical Properties of EVA/MMT Nanocomposites and Their Foams

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**Summary:** In this study, nanocomposites of poly(ethylene-co-vinyl acetate) with two kinds of organically modified montmorillonite (OMMT) were prepared by melt intercalation. Their structures and mechanical properties were characterized by X-ray diffraction (XRD) and tensile test respectively. Especially, foaming of these nanocomposites mixed with chemical blowing agent was carried out through compression molding. Influences of OMMT on foaming ratio and mechanical properties were investigated by density test, tensile test and tear test. Results revealed that both kinds of OMMT with proper content increased tensile strength and Young's modulus of nanocomposites without a compromise of elongation at break. For foaming, OMMTs apparently improved foaming ratio and in particular, one of them can improve tear strength, tensile strength, Young's modulus and elongation although the density was decreased.

**Keywords:** chemical blowing agent; ethylene-vinyl acetate; foaming; modified montmorillonite; nanocomposites

## Introduction

Polymers filled with nanoclay, such as montmorillonites (MMTs), have attracted great interest both in industrial and academic areas. Generally, MMTs are organically modified with surfactants to make them organophilic enough to be compatible with most polymers. Only with a small addition of MMTs (<10 wt%), composites often show unexpectedly great improvement in material properties compared with pristine polymers or conventional composites. These enhanced properties include high modulus,[1–6] decreased gas permeability[7,8] and flammability,[3,9–11] increased heat resistance,[3,4,9,12,13] increased biodegradability of biodegradable polymers.[14,15]

Polymeric foams have broad applications due to their excellent strength/weight ratio, superior thermal and sound insulation abilities, energy absorbing performance.[16] In comparison with conventional fillers, nanometer dimension of nanoclay are especially beneficial for reinforcing foam materials, taking the very thin cell boundary into account. With good dispersion in matrix, the nanometer scale and large surface area of nanoclay provided much more intimate contact between particles, polymer matrix, and gas. Moreover, a higher effective concentration of the fillers can be obtained with a low addition. Both could result in improved nucleation efficiency.[17] Polymer-clay nanocomposites foams prepared using supercritical $CO_2$[17–19] show that well dispersed clay provides a novel way to reduce the cell size and increase cell density. This is particularly beneficial but a very tough procedure for the production of micro or even nanocellular foams. Foaming with chemical blowing agent and compression molding or

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other conventional machines is a convenient production method. Unfortunately, there are few research papers orientated on nanocomposite foams prepared through this way.

Poly(ethylene-co-vinyl acetate) (EVA) is a commonly used polymer which has wide applications, such as packaging films, cable insulating, shoes making, adhesives, and so on. As the vinyl acetate (VA) content increases, the copolymer presents increasing polarity but lower crystallinity, and therefore different mechanical behavior.[20] The increasing polarity with increasing VA content is apparently useful in imparting a high degree of polymer-clay surface interaction and then enhancing the dispersion of clay.[21–23] In this study, EVA/OMMT nanocomposites were prepared through melt mixing with EVA and two types of OMMT. Foaming of these nanocomposites mixed with chemical blowing agent was carried out through compression molding. Effects of OMMT on mechanical properties of EVA/OMMT composites and their foams were investigated.

## Experimental Part

### Materials

EVA copolymers with 18 wt% VA content were supplied by Samsung Total Petrochemicals Co., Ltd. It was dried in vacuum oven to remove moisture at 45 °C for at least 36 hours prior to experiment. Two types of OMMT - Cloisite®15A (C15A) and Cloisite®25A (C25A) were supplied by Southern Clay Products (USA). Table 1 shows the typical properties of the OMMT's. Dicumyl peroxide (DCP) was from Nippon Oil Co. and used as crosslinking agent in foaming. Cellcom-JTR (commercial name, modified Azodicarbonamide) used as foaming agent was supplied from Kum Yang Co. Ltd. (South Korea). The decomposition temperature of it is 145 °C to 157 °C and the gas volume is 160–180 ml/g. All chemicals were used as received.

### Preparation of EVA/OMMT Nanocomposites

EVA was first added into Brabender Plasti-Coder (PLE331) and sheared for 1 minute under the fixed condition. Subsequently, the required amount of OMMT was carefully added within 2 minutes and the compounds were mixed for 9 minutes.

### Preparation of EVA/m-MMT Foams

EVA was first sheared in brabender at 95 °C and a rotor rate of 30 rpm for 2 minutes to get melt. Then the rotor rate was adjusted to 60 rpm followed by the careful addition of required amount of OMMT. After 5-minute mixing, 10 phr foaming agent (Cellcom-JTR) and 1 phr crosslinking agent (DCP) were consequently added into Brabender and for another 4-minute shear-mixing. After being taken out from Brabender, the hot compounds were quickly sheeted by two-roll mill with a roll distance of 1.5 mm. The optimum amount of composite sheet was put into an aluminum mold with a cavity size of 70 × 70 × 2 mm and foaming was carried out by compression-molding under the desired condition (170 °C, 10 MPa, 10 min). After removal of the pressure, expansion took place immediately and the obtained foams were left at room temperature to cool down naturally.

### Characterization

The X-ray diffraction (XRD) measurements were performed at room tempera-

***Table 1.***
Physical Properties of OMMT.

| Code | Commercial Name | Organic Modifier | CEC | % Weight Loss on Ignition |
|---|---|---|---|---|
| C15A | Cloisite®15A | 2M2HT[a] | 125 meq/100 g | 43% |
| C25A | Cloisite®25A | 2MHTL8[b] | 95 meq/100 g | 34% |

[a] dimethyl, dihydrogenatedtallow, quaternary ammonium.
[b] dimethyl, hydrogenatedtallow, 2-ethylhexyl quaternary ammonium.

ture by using SAXSess-Generator (Anton-Paar GmBH, Panalytical, Co.). Intensities from $2\theta = 1.5°–10°$ were recorded using CuK$\alpha$ radiation ($\lambda = 0.154$ nm). $d_{001}$ spacing was calculated using Bragg's law ($\lambda = 2d_{001}\sin\theta$) where $\theta$ is the diffraction angle.

The tensile properties of composites and their foams were measured with a universal testing machine (Instron M4465) according to ASTM D638. The tensile strength, elongation at break and Young's modulus were measured with a specimen gauge length of 25 mm and grip distance of 70 mm. The crosshead speed was 50 mm/min for composites and 500 mm/min for foams. Tear strength of foams were tested using 90° angle test pieces at a crosshead speed of 500 mm/min.

Densities of EVA/OMMT before and after foaming were measured by a densimeter (Mirage Co.) and the foaming ratios were calculated through the following equation: $R = \rho_m/\rho_f$, R: Foaming ratio, $\rho_m$: Density of sample before foaming, $\rho_f$: Density of sample after foaming.

## Results and Discussion

### Dispersion of OMMT

Figure 1 shows the XRD patterns of C15A and EVA/C15A composites with contents of 2 phr, 4 phr, 6 phr individually and the result is generally in accordance with other's studies.[5,24] Pristine C15A has a comparatively apparent intense peak at $2\theta = 2.33°$ ($d_{001} = 3.79$ nm) and two weak peaks at higher diffraction angles. In EVA/C15A composite with 2 phr C15A, there is no apparent diffraction peak existing. This suggests that silicate layers have been exfoliated or intercalated into disordered arrangement by EVA chains and have a random dispersion in matrix. With a content of 4 phr, there is only a weak peak at $2\theta = 4.22°$ which is shifted from (002) and (003) peaks of C15A. It indicates that C15A is mostly in disordered exfoliated or/and intercalated structures as well as only a small part of OMMT sheets are lightly intercalated by EVA chains but become more disordered. However, with a content of 6phr, a diffraction shoulder at $2\theta = 2.17°$ ($d_{001} = 4.09$ nm) and a very wide and less intense peak $2\theta = 4.43°$ are observed. This indicates that with content of C15A increasing, the dispersion is getting poorer. In this case, C15A sheets can not be exfoliated but intercalated and have become more disordered while maintaining an average periodic distance.

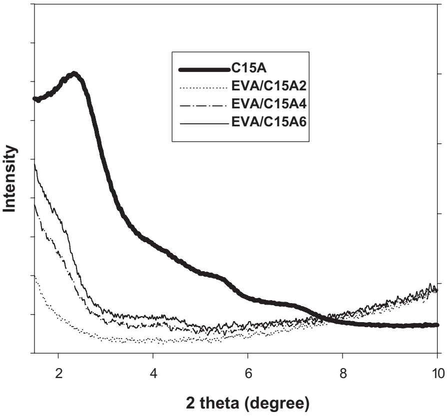

**Figure 1.**
XRD patterns of C15A and EVA/C15A composites prepared by melt blending.

As Figure 2 showing, pristine C25A has a higher shoulder at $2\theta = 4.67°$ (d-spacing = 1.89 nm) which means the d-spacing is lower than that of C15A but arrangement of sheets get much more disordered than

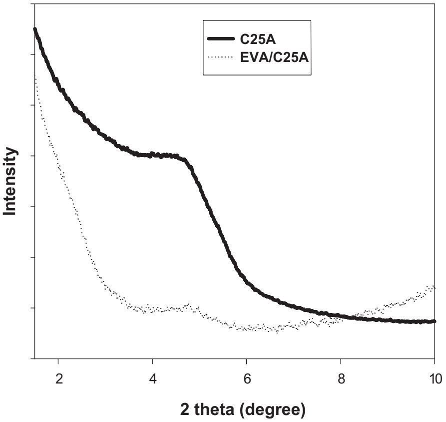

**Figure 2.**
XRD patterns for C25A, Melt blended EVA/C25A4.

that of C15A. In melt blended EVA/C25A4, there is a very weak and broad diffraction peak at the same position of $2\theta = 4.67°$. It can be assumed that in this type of EVA/C25A4 composite, most C25A has been exfoliated or/and intercalated and only a small part still retain the same average d-spacing as pristine C25A does but has become more disordered.

### Mechanical Properties of EVA/OMMT Composites

Figure 3 shows the effects of C15A content on tensile strength and elongation at break of EVA/C15A composites. With such a low addition of C15A as 2 phr, tensile strength is drastically improved in comparison to pure EVA. With further addition of C15A, tensile strength is slightly increased and achieves the peak value at content of 4 phr. This changing trend is in accordance with the dispersions of OMMT with different contents in EVA discussed above. With content of 2 phr, the desired dispersion of C15A results in much more interface area and this provides the essential condition to get excellent interaction between C15A and EVA chains, in other words, the high reinforcement efficiency. With content of C15A increasing, the absolute interface area may be raised but the trend is abated due to the deteriorated dispersion. Therefore, the tensile strength continues to slightly increase with content of C15A increasing but the enhancement efficiency is getting very lower. When content of C15A is over 4 phr, the dispersion is getting much poorer and aggregation possibly begins occurring. It is assumed that the significant dropping of tensile strength is mostly due to diminish of interface area then weaker interaction between C15A and EVA chains.

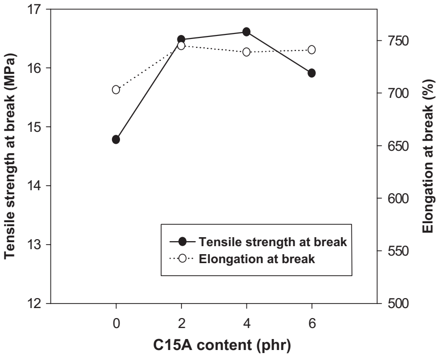

*Figure 3.*
Tensile strength and elongation at break versus C15A content in EVA/C15A composites.

Figure 4 show the effects of type of OMMT on tensile strength and elongation at break of EVA/OMMT respectively. It can be found that C25A has higher enhancement efficiency in tensile strength and elongation than C15A does. According to the composition of organic modifiers used in C15A4 and C25A4, the former has more long aliphatic chains than the latter does. This make C25A is more compatible with EVA which has polarity of a certain degree. Therefore, C25A4 can have stronger interaction with EVA then get a larger volume of entangled clay-polymer entities which could significantly increase the resistance of the composite matrix under stress and, at the same time, align themselves in such a fashion that the external stress is distributed over larger fraction of the polymeric chains.[25] So, C25A4 has higher enhancement in tensile strength even though C15A4 and C25A4 have the similar dispersion in EVA.

For conventional composites, the mechanism that leads to a change in modulus is load transfer.[26] If a high-modulus filler is added to a lower-modulus polymer, the load would transfer from the matrix to the filler, leading to an increase in modulus. Load, i.e. stress, is transferred via a shear stress at the filler/matrix interface. This mechanism underlines the important role of the interface in controlling the modulus of filled polymers. Figure 5 shows the effects of OMMT content on Young's modulus (relative value) of melt blended EVA/C15A. With addition of C15A, Young's modulus of EVA/C15A composite is significantly improved. Especially with C15A content of 6 phr, Young's modulus of composite is nearly 2.4 folds of that of pure EVA. From this figure, we can find the higher enhancement efficiency of OMMT

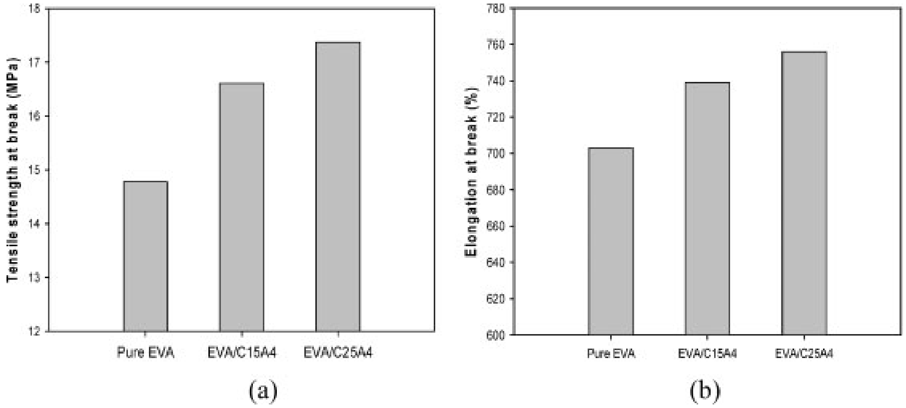

***Figure 4.***
Effects of type of OMMT on tensile strength (a) and elongation at break (b) of EVA/OMMT composites.

in modulus. According to the traditional load-transfer mechanism, the much more interface area and better interaction between well-dispersed OMMT and matrix can result in higher interfacial shear stress and shorter load transfer length then higher efficiency in carrying load and higher composite modulus. Moreover, the higher aspect ratio of OMMT yields the longer length that carries the maximum load then the higher composite modulus.[25]

Figure 6 displays the influence of OMMT type on Young's modulus of melt blended EVA/OMMT composites. An interesting phenomenon can be found that, in the same matrix, C15A shows higher reinforcement efficiency in modulus than C25A does which is contrary to their enhancement in tensile strength at break (C25A has higher efficiency than C15A does). It indicates that the reinforcement mechanism of OMMT for polymers is complicated which maybe involve many factors such as typical properties of OMMT itself, interfacial area, interaction, change of Tg, changes of degree or/and type of crystallinity. As for the present composite systems, considering that EVA matrix has crystallinity of a certain degree and addition of OMMT results in reduction of crystallinity,[22] one reason of the higher

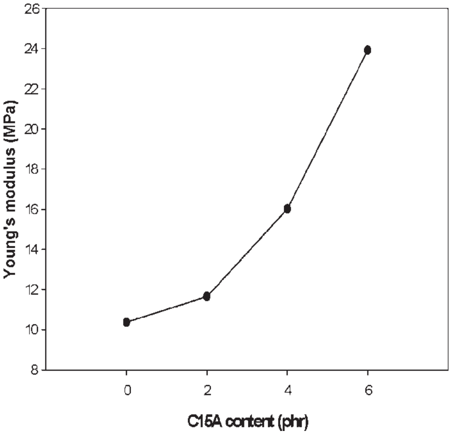

***Figure 5.***
Effects of C15A content on the Young's modulus of EVA/C15A composites.

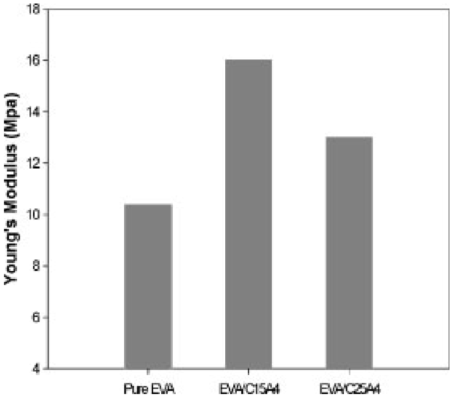

***Figure 6.***
Effects of type of OMMT on Young's modulus of EVA/OMMT composites.

efficiency of C15A in modulus enhancement can be attributed to the comparatively lower reduction of crystalinity in EVA/C15A4 composites. In addition, it is not impossible that the initial modulus of C15A and C25A are different. But both of the two assumptions are left to be testified.

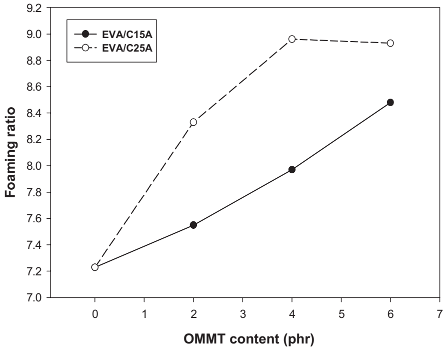

***Figure 7.***
Effects of OMMT content and type on foaming ratio of EVA/OMMT composite foams.

## Foaming Ratio of EVA/m-MMT Composite Foams

Figure 7 shows effect of OMMT content on foaming ratio of EVA/OMMT composite foams. It is well known that,[16] in a heterogeneous liquid system such as polymer with addition of fine solid fillers, the bubbles will usually form more easily at the liquid-solid interface; the bubbles are said to form by a nucleation process, and the solid particles are called nucleating agents. As discussed above, nanometer size, higher aspect ratio and better dispersion of OMMT provides much more interfacial area. It means that there are more opportunities for bubbles to form, in other words, the nucleating efficiency is higher. It is known that[18] the final foam density ($\rho_f$) is generally controlled by the competitive process in the cell nucleation, its growth and coalescence which are strongly affected by the storage and loss modulus of the materials during processing. In the present systems, as more bubbles start to nucleate concurrently, there is a less amount of gas available for bubble growth, leading to a reduction of cell size. Moreover, the increased melt viscosity due to addition of OMMT[27] will hinder the cell growth and lead to a reduced cell size. Generally, addition of OMMT results in smaller cell size but much higher cell density then a reduced foam density, finally the higher foaming ratio.

Figure 8 shows the effects of OMMT content on density and tear strength of EVA/OMMT foams. With OMMT content increasing, the density of EVA/OMMT composite foams are generally decreased, but tear strength of EVA/C15A is always improved, and in case of EVA/C25A, even though the tear strength is first decreased due to decreased density, but when content of C25A is over 4 phr, it is improved along with density slightly changing. These changing trends indicate the good ability of

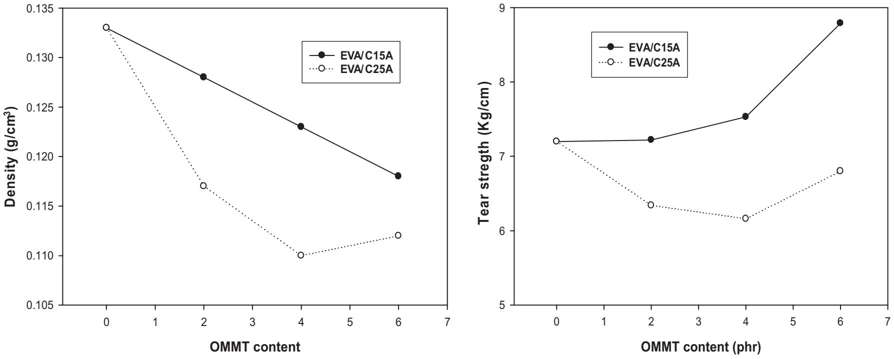

***Figure 8.***
Effects of OMMT content and type on density and tear strength of EVA/OMMT composite foams.

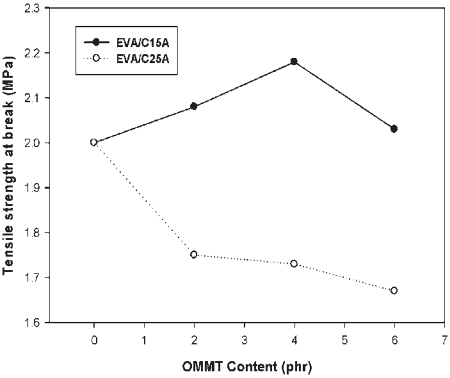

**Figure 9.**
Effects of OMMT content and type on tensile strength at break of EVA/OMMT composite foams.

OMMT to enhance tear strength. The reason can be assumed that, foaming with addition of OMMT may result in smaller cell size and higher cell density. Considering the test point is cut into angle of 90°, in other words, it is a stress concentration point, the smaller cell size and higher cell density can be more effective to diffract stress. In addition, considering the cell boundary is very thin, the nano size of OMMT and good interaction between OMMT and matrix can result fewer defects in solid phase then play an important role in enhancement for tear strength and other properties.

Figure 9 shows the effects of OMMT content on tensile strength at break of EVA/OMMT foams. When content of OMMT is below 4 phr, the tensile strength shows the same changing trend as tear strength, but when over 4 phr, it is decreased due to the deteriorated dispersion of OMMT.

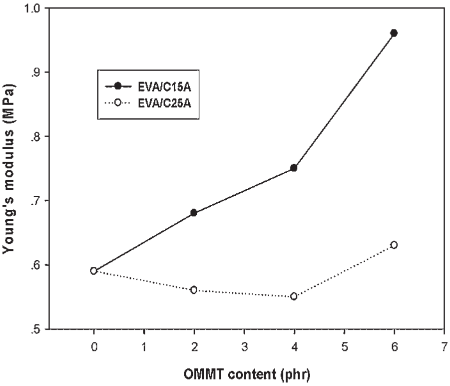

**Figure 10.**
Effects of OMMT content and type on elongation at break of EVA/OMMT composite foams.

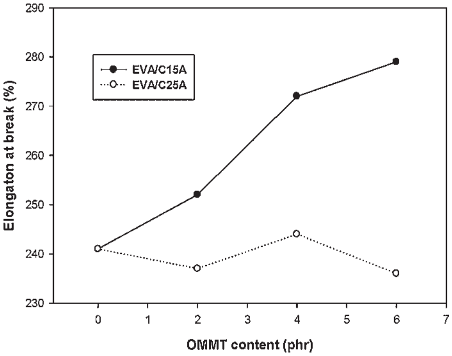

**Figure 11.**
Effects of OMMT content and type on Young's modulus of EVA/OMMT composite foams.

Figure 10 indicates the effects of OMMT content on elongation at break of EVA/OMMT foams. It generally has the same changing trend as tensile strength which means that the higher cell density and smaller cell size, desired dispersion of OMMT in the cell boundary, good interaction between OMMT and matrix can improve tensile strength of foam without a loss of the toughness. Figure 11 shows the significant enhancement ability of OMMT in Young's modulus (relative value) of EVA/OMMT foams. Young's modulus is drastically improved even though the density is decreased. (in case of EVA/C15A foam) or slightly changed at first and then increased (in case of EVA/C25A). Besides the same enhancement mechanism as in composite, there may be an additional effective factor for EVA/OMMT foam that the higher cell density and smaller cell size provide more cell boundary area which is assumed to be important for load transferring.

## Conclusion

EVA/OMMT nanocomposites have been prepared through melt intercalation with EVA and two types of OMMT. Foaming of these composites was also carried out. Dispersion of OMMT in EVA, effects of OMMT on mechanical properties of EVA/OMMT nanocomposites and their foams were investigated. With a low content, Cloisite®15A and Cloisite®25A can be intercalated/exfoliated in matrix EVA by melt blending. For Cloisite®15A, with content ($\leq$6 phr) increasing, the phase was changed from exfoliation to intercalation. Cloisite®25A did not show better dispersion although it was thought to be suitable for polar polymers. Tensile strength at break of EVA/OMMT composite was improved with addition of OMMT and the optimal content was 4 phr in our systems. Young's modulus was significantly improved with increase of OMMT content. Both Cloisite®15A and Cloisite®25A can apparently improve the foaming ratio of EVA/OMMT composites due to their typical physical properties and higher nucleating efficiency. Meanwhile, Cloisite®25A was more effective. Notably, tear strength, elongation and Young's modulus of EVA/OMMT were improved with addition of Cloisite®15A although the density was decreased.

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