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Clay Delamination in Hydrocarbon Rubbers

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Apolar-rubber/clay composites obtained by rubber compounding with pristine and organo-modified montmorillonite (MMT) have been characterized by X-ray diffraction measurements. By reducing the clay content in the rubber, the (00*l*) reflections progressively reduce their intensity, with respect to (*hk*0) reflections, while their spacing remains unaltered. These results indicate the occurrence of a progressive reduction of the number of the packed clay layers without any polymer intercalation. This *delamination* process, different from the usual *intercalation−exfoliation* process, is more efficient for pristine rather than for organo-modified MMT. In particular, pristine MMT, as observed for contents lower than 10% by weight, can be fully delaminated by mixing with natural rubber. Moreover, MMT delaminated by compounding with natural rubber can be aggregated by aging in the presence of suitable organic modifiers (OM), leading to MMT/OM intercalate structures with basal spacing nearly double with respect to the usual MMT/OM intercalate, obtained by direct intercalation of OM in MMT. These results have been rationalized by assuming the formation in the rubber of intercalates comprising organic bilayers rather than organic monolayers.

1. Introduction

Fully exfoliated polymer−clay nanocomposites lead to superior physical properties, thanks to a nanoscale clay dispersion in polymer matrixes and consequent related polymer−clay interactions.[1] However, fully exfoliated polymer−clay nanocomposites are notoriously difficult to attain, particularly in the case of nonpolar polymers.[2]

Moreover, it is common knowledge that clays in the pristine state are miscible only with hydrophilic polymers (e.g., poly(ethylene oxide) and poly(vinyl alcohol)) so that, to render them miscible with hydrophobic polymers, one must exchange the alkali counterions with cationic−organic surfactants, such as alkylammoniums.[1,2] In fact, ionic or polar organic molecules and polymers can interact with clay surface, thus penetrating the interlayer space and expanding the distance between the layers.

According to most reports, the preparation of exfoliated apolar-polymer/pristine-clay nanocomposites by direct compounding has remained an unattained goal. However, in recent years, several papers have appeared in the literature asserting that, in the case of rubbers, intercalation and exfoliation could occur not only with organically modified[3] but also with pristine[4] clays, by simple compounding.

In an attempt to find a possible interpretation of these conflicting literature results, in the present work we have carefully characterized by X-ray diffraction measurements several apolar-rubber/clay systems obtained by simple rubber compounding with pristine and organo-modified montmorillonite (MMT).

2. Experimental Section

Materials. Na^+−MMT clay was purchased from Southern Clay S.p.A. (trade name Cloisite Na), with cationic exchange capacity equal to 92.6 mequiv/100 g. Organically modified clay (trade name Dellite 67G) was from Laviosa Chimica Mineraria S.p.A.: the weight percentages of clay and ammonium moiety were respectively 55 and 45.

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[1] (a) Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T. T.; Kamigaito, O. *J. Mater. Res.* **1993**, *8*, 1179−1185. (b) Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T. T.; Kamigaito, O. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 983. (c) Vaia, R. A; Ishii, H.; Giannelis, E. P. *Chem. Mater.* **1993**, *5*, 1694−1696. (d) Giannelis, E. P.; Krishnamoorti, R.; Manias, E. *Adv. Polym. Sci.* **1999**, *138*, 107−147. (e) Alexandre, M.; Dubois, P. *Mater. Sci. Eng., R: Reports* **2000**, *28*, 1−63. (f) Manias, E.; Touny, A.; Wu, L.; Strawhecker, K.; Lu, B.; Chung, T. C. *Chem. Mater.* **2001**, *13*, 3516−3523.

[2] (a) Robello, D. R.; Tamaguchi, N.; Blanton, T.; Barnes, C. *J. Am. Chem. Soc.* **2004**, *126*, 8118−8119. (b) Choi, Y. S.; Ham, H. T.; Chung, I. J. *Chem. Mater.* **2004**, *16*, 2522−2529. (c) Chou, C.-C.; Lin, J.-J. *Macromolecules* **2005**, *38*, 230−233.

[3] (a) Vu, Y. T.; Mark, J. E.; Pham, L. H.; Engelhardt, M. *J. Appl. Polym. Sci.* **2001**, *82*, 1391−1403. (b) Usuki, A.; Tukigase, A.; Kato, M. *Polymer* **2002**, *43*, 2185−2189. (c) Arroyo, M.; Lopez-Manchado, M. A.; Herrero, B. *Polymer* **2003**, *44*, 2447−2453. (d) Lopez-Manchado, M. A.; Herrero, B.; Arroyo, M. *Polym. Int.* **2004**, *53*, 1766−1772. (e) Zheng, H.; Zhang, Y.; Peng, Z. Zhang, Y. *J. Appl. Polym. Sci.* **2004**, *92*, 638−646.

[4] (a) Sadhu, S.; Bhowmick, A. K. *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 1573−1585. (b) Sadhu, S.; Bhowmick, A. K. *Adv. Eng. Mater.* **2004**, *6*, 738−742.

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Ammonium salt di(hydrogenated tallow)-dimethylammonium chloride was purchased from Akzo Nobel (trade name Arquad HC Pastilles) with a chemical purity of 96%. Synthetic *cis*-polyisoprene rubber was from Nizhnekamskneftechim Export (trade name SKI3). Natural rubber was from Lee Rubber (trade name SMR GP).

Mooney viscosity of both synthetic and natural polyisoprenes was determined with a Mooney MV 2000 E viscometer from Alpha Technologies, following the experimental procedure described by ASTM D1646. In particular, the test was run at 100 °C, using a rotor with a 38.10 mm diameter rotating at 0.209 rad/s. Rubber samples were preheated for 1 min at 100 °C, and the rotor was allowed to rotate for 4 min before measuring the viscosity value, indicated in Mooney units (MU). Mooney viscosity (ML(1 + 4)-100 °C) of synthetic and natural isoprene rubber was found to be 70 MU and 62 MU, respectively, thus indicating a slightly higher molecular mass for the synthetic rubber.

Composites Preparation. Composites were prepared in a Haake PolyLab internal mixer with a 180 mL mixing room.

(Organically Modified) Clay/Rubber Composites. Preparation of a composite with synthetic polyisoprene and 20 phr (parts per hundred of rubber) of Dellite 67G is reported as an example. A total of 150 g of synthetic polyisoprene was put in the mixer at 80 °C, and after 1 min of rubber mastication, 30 g of organoclay Dellite 67G was added. Mixing was carried out for 5 min, and the compound was discharged at a temperature of 115 °C. The content of organoclay in the composite was 16.7% by weight (wt %).

Clay/Organic Modifier/Rubber Composites. Preparation of a composite with natural rubber is reported as an example. A total of 150 g of natural rubber was put in the mixer at 80 °C, and after 1 min of rubber mastication, 16.5 g of clay and 13.5 g of ammonium salt were added. Mixing was carried out analogously to the method reported above.

Composites Characterization. Wide-angle X-ray diffraction (WAXD) patterns with nickel filtered Cu Kα radiation were obtained, in reflection, with an automatic Bruker D8 Advance diffractometer. The intensities of the WAXD pattern, after subtraction of the tail of the primary beam, have been corrected for polarization and Lorentz factors, by using the following formula:

$$I_{\mathrm{cor}} = I_{\mathrm{exp}}/\{[(1 + \cos^2 2\theta)/2][(\sin^2 \theta \cos \theta)/2]\}$$

wherein I_{cor} is the corrected peak intensity, I_{exp} is the peak experimental intensity, and 2θ is the peak diffraction angle.

3. Results and Discussion

3.1. Clay/Rubber Composites. The X-ray diffraction (Cu Kα) patterns in the 2θ range 2−80° of pristine MMT before and after compounding with 1,4-*cis*-polyisoprene rubber (20 phr, 16.7 wt %) are shown in Figure 1A,B, respectively. The amorphous diffraction halo of the rubber is shown for comparison in Figure 1B′. The pattern obtained by subtracting the rubber pattern from the compound pattern (i.e., B − B′) is shown in Figure 1C.

A comparison between the pristine clay pattern (A) and the subtraction pattern (C) clearly shows that, as a consequence of compounding, (00*l*) peaks corresponding to periodicities perpendicular to the structural layers reduce their intensity with respect to the other clay reflections. For instance, the intensity of the (001) reflection (evaluated as peak area, inset of Figure 1) decreases of nearly 80% with respect to both (020) and (060) reflections, corresponding to $d = 0.45$ and 0.15 nm, respectively.

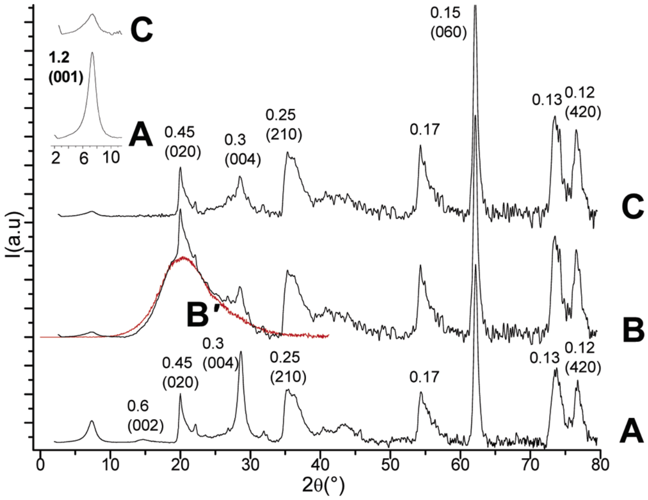

Figure 1. X-ray diffraction (Cu Kα) patterns in the 2θ range 2−80° of (A) pristine MMT; (B) compound of polyisoprene rubber with 20 phr of clay; (B′) polyisoprene rubber; and (C) the pattern obtained by subtracting the rubber pattern B′ from the compound pattern B. The *d* spacings (in nanometers) and the Miller indices of the most relevant clay reflections are indicated. The inset enlarges the (001) peak.

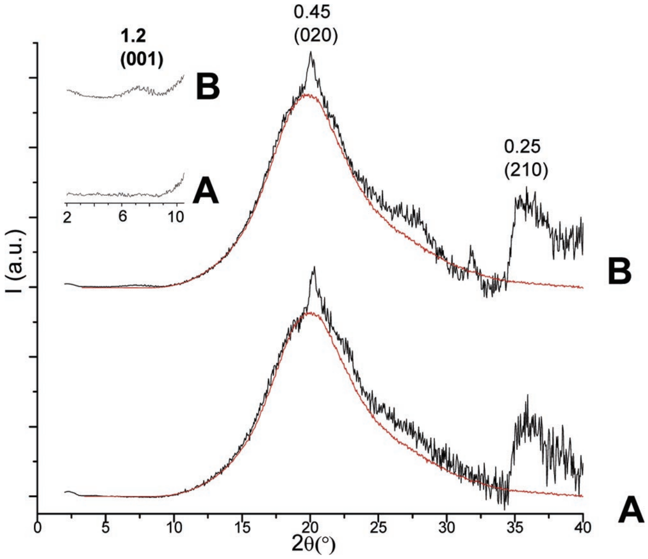

Figure 2. X-ray diffraction (Cu Kα) patterns in the 2θ range 2−40° of compounds obtained by mixing of natural rubber and pristine MMT: (A) 7 phr and (B) 10 phr.

This phenomenon more clearly appears for compounds with lower clay content. For instance, X-ray diffraction patterns in the 2θ range 2−40° of natural rubber compounds with 7 phr (6.5 wt %) and 10 phr (9.1 wt %) are shown in Figure 2A,B, respectively.

The patterns of Figures 1 and 2 show that a progressive broadening and reduction of intensity of (00*l*) MMT peaks can occur as a consequence of compounding of pristine MMT with all considered apolar rubbers. For low MMT content a nearly complete disappearance of the (00*l*) peaks occurs, while the other MMT peaks essentially maintain their intensity. This clearly indicates the occurrence of a phenomenon of clay delamination.

It is worth noting that the (001) reflection, also when barely detectable (e.g., inset B of Figure 2), always maintains the same spacing ($d = 1.2$ nm).

What is reported in Figure 1 seems to indicate that, contrary to the case of the usually observed exfoliation

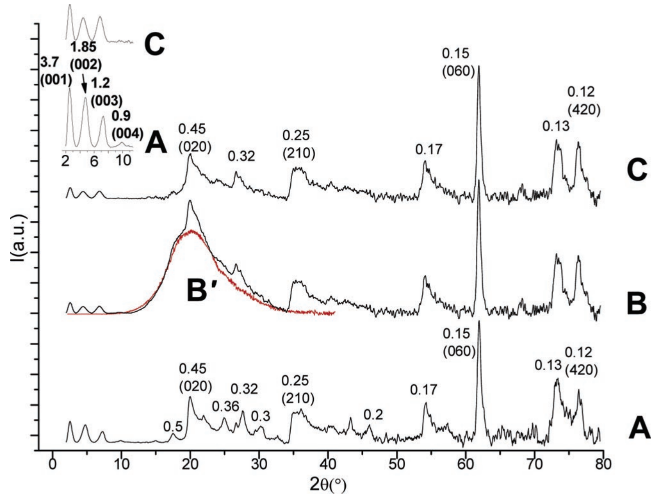

Figure 3. X-ray diffraction (Cu Kα) patterns in the 2θ range 2−80° of (A) a MMT modified by di-talloyldimethylammonium chloride $Cl^-(Me_2T_2N)^+$; (B) compound of polyisoprene rubber with 20 phr of organo-modified clay; (B′) polyisoprene rubber; and (C) the pattern obtained by subtracting the rubber pattern B′ from the compound pattern B. The d spacing (in nanometers) and the Miller indices of the most relevant clay reflections are indicated.

phenomena, the present delamination phenomena would occur without any preliminary intercalation.

3.2. Organically Modified Clay/Rubber Composites. The X-ray diffraction pattern in the 2θ range 2−80° of a MMT where the alkali counterions have been exchanged with a cationic−organic modifier (di(hydrogenated tallow)dimethylammonium chloride, $Cl^-(Me_2T_2N)^+$, thereafter OM) is shown in Figure 3A. The presence of (00l) reflections, with $1 \leq l \leq 4$ for a periodicity of nearly 3.7 nm, clearly indicates the formation of an intercalate crystalline structure between clay and the organic modifier, whereas the presence of higher order (00l) reflections indicates a regular distribution of the alkylammonium cations in the interlayers. It is worth adding that the basal spacing is larger than the one observed for intercalate MMT structures with dimethyldioctadecylammonium chloride (2.4−3.0 nm),[5] which are characterized by very weak, if any, higher order (00l) reflections[5] and hence by lower order in the alkylammonium distribution.

The X-ray diffraction pattern of a 1,4-*cis*-polyisoprene rubber after compounding with the modified-clay of Figure 3A (20 phr) is shown in Figure 3B while the pattern obtained by subtracting the rubber pattern from the compound pattern (i.e., B − B′) is shown in Figure 3C.

As for the pristine clay, as a consequence of rubber compounding, (00l) peaks remain in the same positions ((001), (002), and (003) peaks at $d = 3.7$, 1.8(5), and 1.2(3) nm, respectively). However, their intensity reduction with respect to the other clay reflections are less pronounced than for pristine clay. For instance, the intensity reduction of the (002) and (003) reflections is lower than 40%, with respect to both the (020) and (060) reflections.

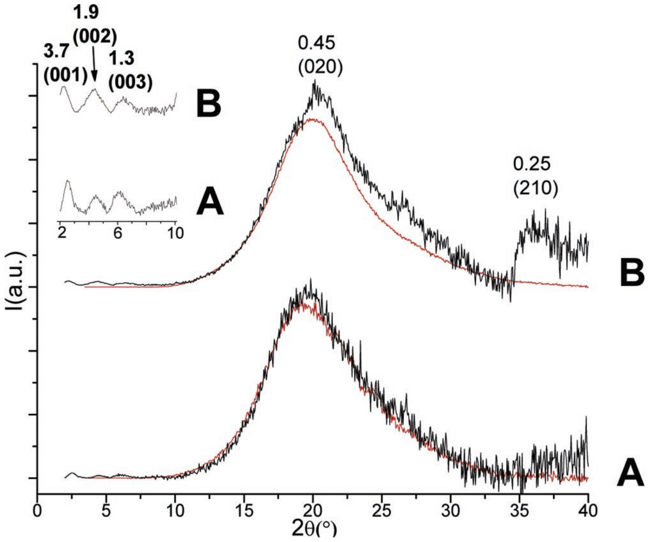

Figure 4. X-ray diffraction (Cu Kα) pattern in the 2θ range 2−40° of apolar-rubber/modified-MMT compounds obtained by mixing (A) polyisoprene/modified MMT, 7 phr, and (B) natural-rubber/modified MMT, 10 phr.

The intensity reduction of the (00l) peaks remains lower than 40% also for compounds with clay content lower than 10 phr (Figure 4).

3.3. Clay/Organic Modifier/Rubber Composites. In this section, composites obtained by mixing an isoprene rubber with pristine MMT and a cationic−organic surfactant have been characterized. Significantly different results have been obtained using synthetic or natural polyisoprene.

3.3.1. Clay/Organic Modifier/Synthetic Polyisoprene−Rubber Composites. The X-ray diffraction pattern of a compound containing 1,4-*cis*-polyisoprene rubber, 6.6 phr of pristine MMT, and 5.4 phr of the cationic surfactant OM already used as organic modifier of MMT is shown in Figure 5A.

The most interesting feature of this pattern is the appearance of several peaks for $2\theta < 10°$, which can be interpreted as (00l) peaks, with $1 \leq l \leq 4$, for a periodicity of nearly 3.8 nm. These peaks are not present in pristine MMT (Figure 1A) while they are similar to those observed for the organic-modified clay. This result clearly indicates that an intercalate crystalline structure between a clay and an organic modifier can be obtained by mixing them in an apolar rubber. The intercalated organically modified clay is similar to the one commercially available, obtained by reacting pristine clay with OM.

3.3.2. Clay/Organic Modifier/Natural Rubber Composites. X-ray diffraction patterns of freshly prepared compounds of natural rubber with pristine MMT and OM are similar to those observed for compounds with only pristine MMT. Just as an example, the X-ray diffraction pattern of a freshly prepared compound of natural rubber with 6.6 phr (5.9 wt %) of pristine MMT and 5.4 phr (4.8 wt %) of OM (Figure 5B) is very similar to those of simple rubber/pristine-clay compounds (see, e.g., Figure 2A). In particular, the pattern of Figure 5B shows the presence of the (020) and (210) MMT peaks and the disappearance of the (001) and (004) peaks, clearly indicating the occurrence of the delamination phenomenon, which has been described in section 3.2.

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[5] (a) Ogawa, M.; Aono, T.; Kuroda, K.; Kato, C. *Langmuir* **1993**, *9*, 1529−1533. (b) Moraru, V. N. *Appl. Clay Sci.* **2001**, *19*, 11−26. (c) Osman, M. A.; Ploetze, M.; Skabal, P. *J. Phys. Chem. B* **2004**, *108*, 2580−2588. (d) Osman, M. A.; Ernst, M.; Meier, B. H.; Suter, U. W. *J. Phys. Chem. B* **2002**, *106*, 653−662.

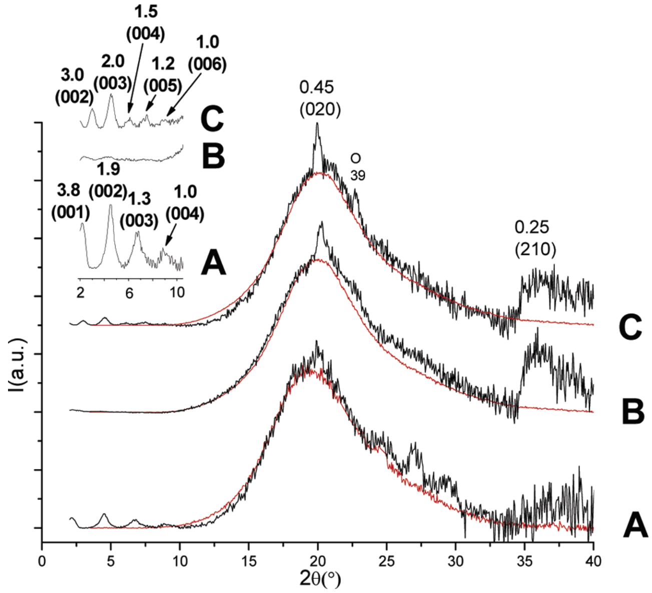

Figure 5. X-ray diffraction (Cu Kα) pattern in the 2θ range 2−40° of compounds obtained by mixing of pristine MMT, the organic modifier (OM), and an apolar rubber: (A) 1,4-*cis*-polyisoprene, MMT (6.6 phr), OM (5.4 phr); (B) natural rubber, MMT (6.6 phr), OM (5.4 phr), freshly prepared; and (C) B after a few months of aging at room temperature.

However, the X-ray diffraction patterns of these natural-rubber/MMT/OM compounds change significantly with their aging, because several crystalline peaks progressively appear. In particular, the rubber compound of Figure 5B, after a few months of aging at room temperature, presents the X-ray diffraction pattern of Figure 5C that shows diffraction peaks which can be interpreted as (00l) reflections, with $2 \leq l \leq 6$, for a periodicity of nearly 6.0 nm. The same periodicity is observed, after aging, for other natural-rubber/MMT/OM compounds having different compositions.

In summary, a pristine clay is delaminated by compounding with natural rubber while the presence in the rubber compound of a suitable organic modifier brings about with aging the formation of a clay/OM intercalate structure. However, this clay/OM intercalate structure presents a distance between clay layers being nearly double with respect to the one observed for direct intercalation of OM in MMT.

3.3.3. Possible Interpretation of the Different Behaviors of Synthetic and Natural Polyisoprene. The behavior described in section 3.3.1, that is, the formation of the usual MMT/OM intercalate phase (with interlayer distance in the range 3.7−3.8 nm) for the synthetic rubber compounds, indicates that the rubber acts simply as a solvent of OM, that is, as a reaction medium for clay−OM interaction, thus favoring OM intercalation in the clay with the formation of the same intercalate structure that could be obtained in a low molecular mass solvent.

The behavior described in section 3.3.2, that is, the clay delamination after compounding with natural rubber and OM, indicates that the kinetics of OM diffusion in the clay is slower than the kinetics of clay delamination. Moreover, the formation, after aging of these compounds, of a new kind of MMT/OM intercalate phase, with a nearly double interlayer distance (6.0 nm), suggests that the clay layers, possibly covered by the organic surfactant, on both basal faces tend to re-aggregate.

In this respect, it is worth adding that each layer has a thickness of nearly 1 nm, while the longest molecular axis of a dimethyldioctadecylammonium molecule in its preferred conformation is approximately 2.6 nm and the corresponding bimolecular arrangement measures about 5.0 nm.[5d] Hence, the observed basal-plane spacings (d_{001}) could be simply rationalized by intercalate crystal structures presenting paraffin-type monolayers ($d \approx 1 + 2.6$ nm ≈ 3.6 nm) and bilayers ($d \approx 1 + 5.0$ nm ≈ 6.0 nm), by assuming orientation of the alkyl chains nearly perpendicular to the inorganic layers. This structural hypothesis well agrees with the procedures used to obtain the different intercalates. In fact, the supposed intercalate monolayer structures are obtained by OM intercalation in the ordered clay, while the supposed intercalate bilayer structures are obtained as a consequence of re-aggregation of delaminated clay layers.

The occurrence of clay/OM intercalation for composites with the synthetic rubber and clay delamination for composites with the natural rubber could be due to the largely different polarity. It is well-known[6] that natural rubber includes a large amount of polar substances: “true rubber” is not more than 94%, and proteins and neutral and polar lipids are the main minor ingredients (nearly 2%, 2%, and 1% by weight, respectively).

4. Conclusions

The intensities of (00l) clay reflections can be drastically reduced with respect to the intensities of (hk0) reflections, as a consequence of mixing with apolar rubbers. In particular, (00l) reflections of a pristine clay become undetectable for composites with low clay content (≤7 phr). Correspondingly, the (00l) spacings (when detectable) remain unaltered with respect to those of unmixed clays, as schematically represented in Figure 6A.

It is well-known that the disappearance of (00l) clay reflections, often observed for composites between polar polymers and organo-modified clays, is instead preceded by progressive shifts to lower diffraction angles of (00l) clay reflections (as schematically represented in Figure 6B), clearly indicating the occurrence of clay intercalation with polar polymer molecules, eventually leading to clay exfoliation.

These results indicate that complete separation between clay layers can be achieved not only by the well-known *intercalation−exfoliation* mechanism but also by a *delamination* process, involving a progressive reduction of the number of the packed clay layers without any polymer intercalation. This delamination process is presently observed for clay composites with apolar rubbers while the intercalation−exfoliation mechanism preferably occurs for clay composites with polar polymers.

The described delamination process is more efficient for pristine clays rather than for organo-modified clays (Figures 1−4), while the intercalation−exfoliation mechanism is more efficient (and often operates only) for organo-modified clays.

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(6) (a) Chapman, A. V. Presented at Elastomers 2001, First EPF School, XXIII M. Farina, AIM School, Gargnano (BS), Italy, June 4−8, 2001. (b) Brosse, J. C.; Campistron, I.; Derouet, D.; Reyx, D. *L'Actualitè Chimique* **2002**, *11−12*, 45−51.

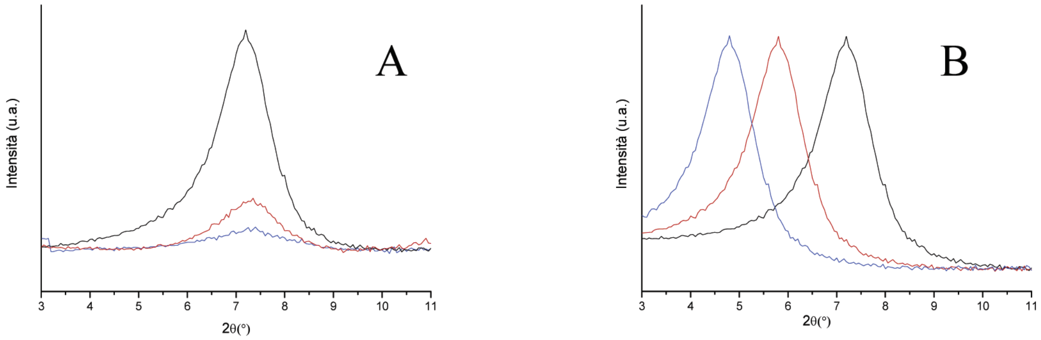

Figure 6. A schematic representation of progressive changes which can occur to the (001) reflection of a clay as a consequence of mixing with polymer matrixes: (A) clay delamination, without polymer intercalation, which we discuss in the present paper; (B) clay intercalation with polymer molecules eventually leading to clay exfoliation, typical of mixing of polar polymers with organo-modified clays. Rather surprisingly, this clay delamination mechanism is more efficient for pristine MMT than for organo-modified MMT.

The occurrence in suitable conditions of complete clay delamination (i.e., leading to isolated clay layers) in composites with apolar rubbers has also been confirmed by compounding pristine clays with natural rubber, in the presence of alkylammonium modifiers (OM). In fact, the obtained composites, when freshly prepared, do not show any (00*l*) diffraction peak while, after aging, present several (00*l*) peaks, indicating the formation of MMT/OM intercalate with basal spacing (6.0 nm) nearly double with respect to the usual MMT/OM intercalate, obtained by direct intercalation of OM in MMT (3.7 nm).

This large basal spacing suggests that the MMT/OM intercalate, formed in rubber from the delaminated clay, comprises organic bilayers rather than monolayers.

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