Preparation of EPDM/synthetic montmorillonite nanocomposites by direct compounding

C. DA SILVA
Institut de Chimie des Surfaces et Interfaces, CNRS UPR 9069, Université de Haute Alsace, 15 rue Jean Starcky, BP 2488, 68057 Mulhouse, France; Laboratoire de Matériaux Minéraux, CNRS UMR 7016, Ecole Nationale Supérieure de Chimie de Mulhouse/Université de Haute Alsace, 3 rue Alfred Werner, 68093 Mulhouse, France

B. HAIDAR*, A. VIDAL
Institut de Chimie des Surfaces et Interfaces, CNRS UPR 9069, Université de Haute Alsace, 15 rue Jean Starcky, BP 2488, 68057 Mulhouse, France
E-mail: b.haidar@uha.fr

J. MIEHE-BRENDLE, R. LE DRED
Laboratoire de Matériaux Minéraux, CNRS UMR 7016, Ecole Nationale Supérieure de Chimie de Mulhouse/Université de Haute Alsace, 3 rue Alfred Werner, 68093 Mulhouse, France

L. VIDAL
Institut de Chimie des Surfaces et Interfaces, CNRS UPR 9069, Université de Haute Alsace, 15 rue Jean Starcky, BP 2488, 68057 Mulhouse, France

Elastomers are usually compounded with fillers such as carbon black or silica in order to improve their mechanical properties. The idea of using clays as fillers in a polymer matrix appeared in the 1950s, but not until 1990 did the Toyota group find that clay layers could be intercalated or exfoliated by polyamide-6 macromolecules [1]. Such composites can be expected to provide a very high interaction area between the filler and the polymer and as a consequence possess improved properties as compared to traditional reinforcing fillers.

Many nanocomposites based on polymer/clay blends have been investigated using different polymers compounded in the melt such as polyamide-6 [1], polyethylene [2], polypropylene [3], poly(ethylene oxide) [4] and polystyrene [5]. However, relatively little attention has been paid to conventional rubbery materials. Such nanocomposites have been generally prepared by latex compounding [6, 7], solution blending [8, 9] or by using an appropriate vulcanization system [10], but no evidence of exfoliated rubber/clay nanocomposites prepared by direct compounding of the clay with the elastomer has been reported up to now in the litterature, except in the special case of silicone networks [11, 12]. Although thermoplastics are considered as rubbery when compounded in the melt, true elastomers at moderate temperature differ from melted thermoplastics by their high viscosity. This explains the complications to achieve clay exfoliation in elastomer matrices.

The aim of this study is to define the main parameters controlling clay intercalation and exfoliation in an elastomer matrix, in order to prepare composites structured at the nanometer scale. Furthermore, we chose to respect three conditions: (1) no solvent use in the blend, (2) maximum exfoliation to a single layer level, (3) accurate understanding of the composite structure. Therefore, the use of a tailored clay pre-treatment with an appropriate polymer may assist the complete exfoliation by direct compounding process, even in a high viscosity rubbery medium. The use of synthetic clays may enable, moreover, the control of both chemical composition and purity. This would provide a real advantage as compared to natural clays that are generally used in studies described in the literature. Impurities, in particular, can be considered as a source of heterogeneity in the clay treatment and consequently in the exfoliation heterogeneity as well.

Both elastomers used as matrices were commercial forms of Ethylene Propylene Diene Monomer (EPDM). Maleic Anhydride grafted EPDM (EPDMgMA, MA content 1 wt%) was Royaltuf 498 by Uniroyal Chemicals (ethylidene 2,5 norbornene, $E/P = 55/45\%$, $M_w = 110000$ determined by GPC). Unmodified EPDM was Nordel 1440 from Du Pont (1,4 hexadiene, $M_w = 400000$). Polymers were purified by dissolving in cyclohexane. Only the soluble fractions were dried and used.

The clays were synthesized using commercial reagents. The sodium form of montmorillonite-type [$Na_{0.3}(Al_{1.7}Mg_{0.3})Si_4O_{10}(OH)_2$] clay (Mmt) was prepared by hydrothermal synthesis in hydrofluoric medium at 220 °C for 48 hrs in a stainless steel PTFE lined autoclave [13]. In order to convert such clay into an organophilic material for a better dispersion in the elastomer matrix, the silicate was then treated by cation exchange using an aqueous solution of octadecyltrimethylammonium bromide C_{18}TMABr (Aldrich), under vigorous stirring for 24 hrs. The resulting organoclay was washed 3 times with distilled water, and dried for 48 hrs at 60 °C. The amount of intercalated $C_{18}TMA^+$ was controlled by the concentration

---

* To whom correspondence should be addressed.

TABLE I Basal distance (d_{001}) and organic content of the as-synthesized and the organically modified montmorillonites

Sample	d_{100} (nm)	Organic content (%)
Mmt	1.34	0
OMmt1	1.43	16
OMmt2	1.97	25
OMmt3	4.10	48

of the reacting solution. The montmorillonite was also treated with increasing C_{18}TMABr concentrations: 8.2×10^{-3} M for OMmt1, 1.6×10^{-2} M for OMmt2 and $6.4.10^{-2}$ M for OMmt3 (50.10^{-6} m^3 of treatment solution per gram of clay), corresponding to respectively 0.5, 1 and 4 times the amount of exchangeable Na^+ ions. Organic contents were determined by thermogravimetric analysis. Results are reported in Table I.

Composites with a 4 wt% of mineral content were prepared by a direct compounding process of the layered silicate with the elastomer for 20 min at 80 °C and 30 rpm in a Brabender Plasticorder PLE651 internal mixer. Composites were finally molded into 0.5 mm thick regular sheets (80 °C, 10 mn, 50 MPa).

Wide angle X-ray diffraction (XRD) data were collected with a Philips X'Pert diffractometer using Cu K_α radiation (0.154 nm, 40 kV, 20 mA) in a Bragg geometry at room temperature. Nanocomposite morphology was directly observed by Transmission Electron Microscopy (TEM, Philips CM 200, acceleration voltage of 200 kV). Ultrathin sections (less than 100 nm) were prepared with a diamond knife using an ultramicrotome LKB 8800 Ultrotome III under cryogenic conditions.

Table I provides the basal distance (d_{001}, related to the extent of the interlayer spacing) and the organic content of the as-synthesized and the organically modified montmorillonites used in this study.

Three types of organo-modified montmorillonites are reported in Table 1: OMmt1, OMmt2, and OMmt3 with increasing organic content and interlayer spacing as compared to the unmodified synthetic montmorillonite Mmt. The shift of diffraction peaks to lower angle values indicates an increase of the interlayer spacing, that is related to the amount and the arrangement [14] of intercalated $C_{18}TMA^+$ cations.

Visual observation of molded composite sheets shows that opacity decreases with increasing organic treatment. This proves that the particle dispersion is at least improved by organic treatment. The influence of organic treatments on the exfoliation degree of the clay in the grafted EPDM matrix was investigated by XRD and TEM analysis. XRD characterization is generally based on the comparison between the diffraction peak position of the organoclay powder and the organoclay dispersed in the polymer matrix [15]. In our study, we compared the diffraction peak position between the organoclay in an unmodified EPDM and in the MA grafted one, at the same filler content (4 wt%). The unmodified EPDM composite should be a better reference, since the same experimental settings can be used. Furthermore, variation of the peak diffraction intensity can be correlated to the exfoliation extent of the clay [16].

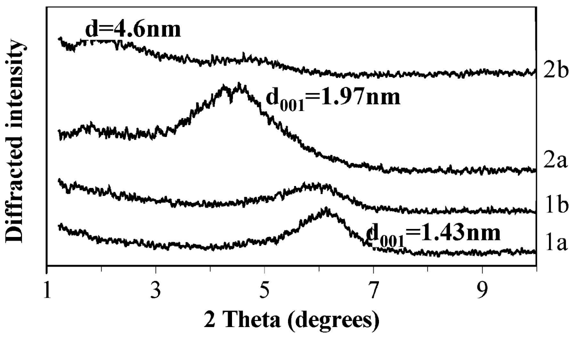

Figure 1 X-ray diffraction patterns of elastomer/montmorillonite composites: EPDM/OMmt1 (1a), EPDMgAM/OMmt1 (1b), EPDM/OMmt2 (2a), and EPDMgAM/OMmt2 (2b).

For the organo-modified montmorillonite with poor interlayer spacing (OMmt1), the XRD pattern of the composite exhibits weak change of the basal diffraction peak intensity (Fig. 1), suggesting that nanocomposite structure is not achieved. This is confirmed by TEM which shows primary clay particles in the matrix, with nevertheless a good microscale dispersion. In this case, organic treatment acts as a filler/polymer compatibilizer.

For the medium interlayer spacing (OMmt2), the basal diffraction peak is shifted to lower angle values, corresponding to an increase of the interlayer spacing to 4.6 nm (Fig. 1). Therefore, elastomeric macromolecules are most likely intercalated between clay layers yielding an ordered multilayer morphology. This structure has been confirmed by TEM observation of the nanocomposite.

In the case of the highest organic treatment (OMmt3), no more basal diffraction peak is visible in the XRD diffractogramm of the EPDMgAM/OMmt3 nanocomposite, showing that the montmorillonite layers have lost their ordered multilayer structure (Fig. 2). This result suggests at least partial exfoliation of the clay in the rubber. The exfoliated nanocomposite formation is clearly confirmed by TEM in Fig. 3, in which the result obtained on EPDMgAM/OMmt3 is compared with the EPDM/OMmt3 composite used as a reference. It is unambiguously obvious that unmodified polymer does not allow the exfoliation of an even modified clay. In this case, clay treatment improves, at the very best, the microscale aggregate dispersion.

In summary, exfoliated nanocomposites EPDM/clay nanocomposites have been prepared by a direct

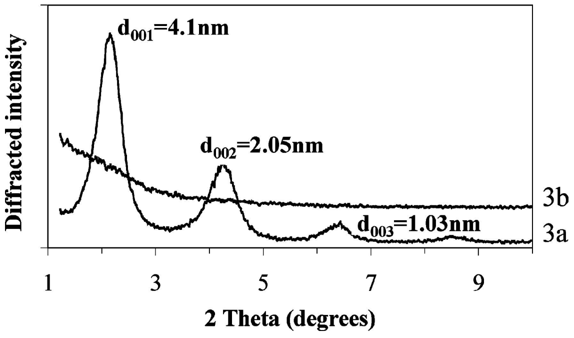

Figure 2 X-ray diffraction patterns of EPDM/OMmt3 (3a) and EPDMgAM/OMmt3 (3b) 4 wt% composites.

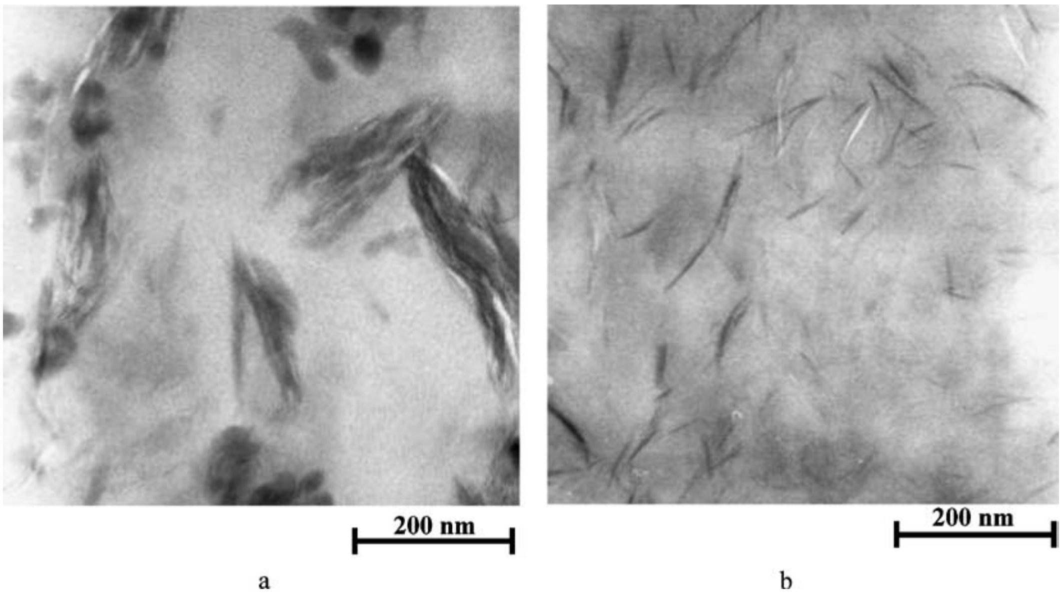

Figure 3 Transmission electron micrograph of the EPDM/OMmt3 (a) and EPDMgMA/OMmt3 (b) 4 wt% nanocomposites.

compounding process, using synthetic montmorillonite with controlled structure and composition. Moreover, the composite morphology (non-intercalated microcomposite, intercalated or exfoliated nanocomposite) is controlled by the organic alkylammonium treatment of the montmorillonite. Such non-crosslinked exfoliated systems should allow a better understanding of the influence of elastomer/clay interactions on structural and mechanical properties. The influence of the clay structure on the exfoliation extent will be presented in a forthcoming paper.

References

1. A. OKADA, M. KAWASUMI, A. USUKI, Y. KOJIMA, T. KURAUCHI and O. KAMIGAITO, *Mater. Res. Soc. Proc.* **45** (1990) 171.
2. K. H. WANG, M. XU, Y. S. CHOI and I. J. CHUNG, *Polym. Bull.* **46** (2001) 499.
3. X. LIU and Q. WU, *Polymer* **42** (2001) 10013.
4. J. BUJDAK, E. HACKETT and E. P. GIANNELIS, *Chem. Mater.* **12** (2000) 2168.
5. Y. K. KIM, Y. S. CHOI, K. H. WANG and I. J. CHUNG, *ibid.* **14**(12) (2002) 4490.
6. L. ZHANG, Y. WANG, Y. WANG, Y. SUI and D. YU, *J. Appl. Polym. Sci.* **78**(11) (2000) 1873.
7. Y. WANG, L. ZHANG, C. TANG and D. YU, *ibid.* **78**(11) (2000) 1879.
8. M. GANTER, W. GRONSKY, P. REICHERT and R. MÜLHAUPT, *Rubb. Chem. Techn.* **74** (2001) 221.
9. S. JOLY, G. GARNAUD, R. OLLITRAULT and L. BOKOBZA, *Chem. Mater.* **14** (2002) 4202.
10. A. USUKI, A. TUKIGASE and M. KATO, *Polymer* **43** (2002) 2185.
11. S. D. BURNSIDE and E. P. GIANNELIS, *Chem. Mater.* **7**(9) (1995) 1597.
12. P. C. LEBARON and T. J. PINNAVAIA, *ibid.* **13** (2001) 3760.
13. M. REINHOLDT, J. MIEHE-BRENDLE, L. DELMOTTE, M.-H. THUILLIER, R. LE DRED, R. CORTES and A.-M. FLANK, *Eur. J. Inorg. Chem.* (2001) 2831.
14. G. LAGALY, *Sol. Stat. Ion.* **22** (1986) 43.
15. E. MANIAS, A. TOUNY, L. WU, K. STRAWHECKER, B. LU and T. C. CHUNG, *Chem. Mater.* **13** (2001) 3516.
16. R. A. VAIA, K. D. JANDT, E. J. KRAMER and E. P. GIANNELIS, *Macromolecules* **28** (1995) 8080.

Received 6 April
and accepted 29 July 2004