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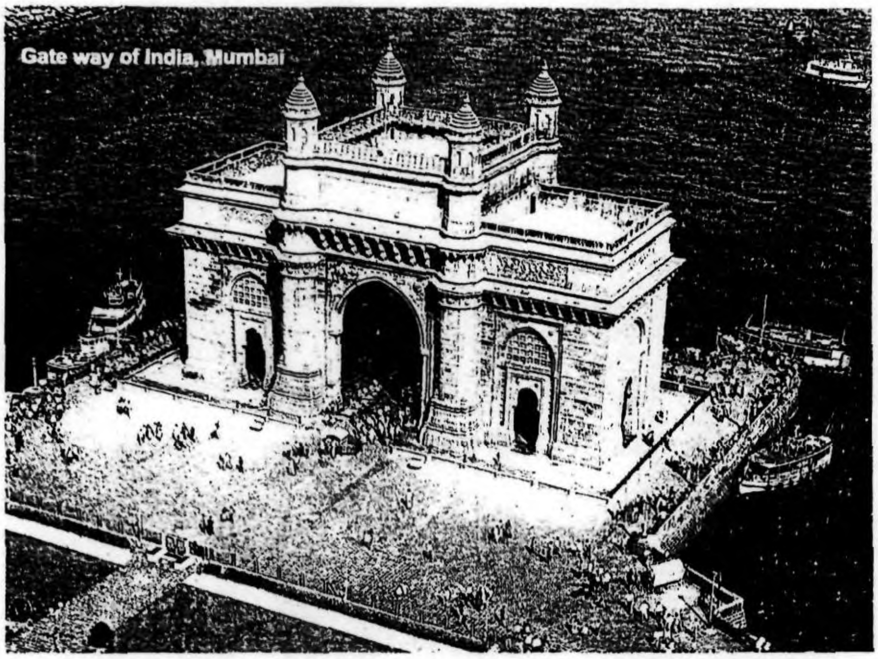

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Natural Rubber Nanocomposites : Structure Property Relationships

(EA-028)

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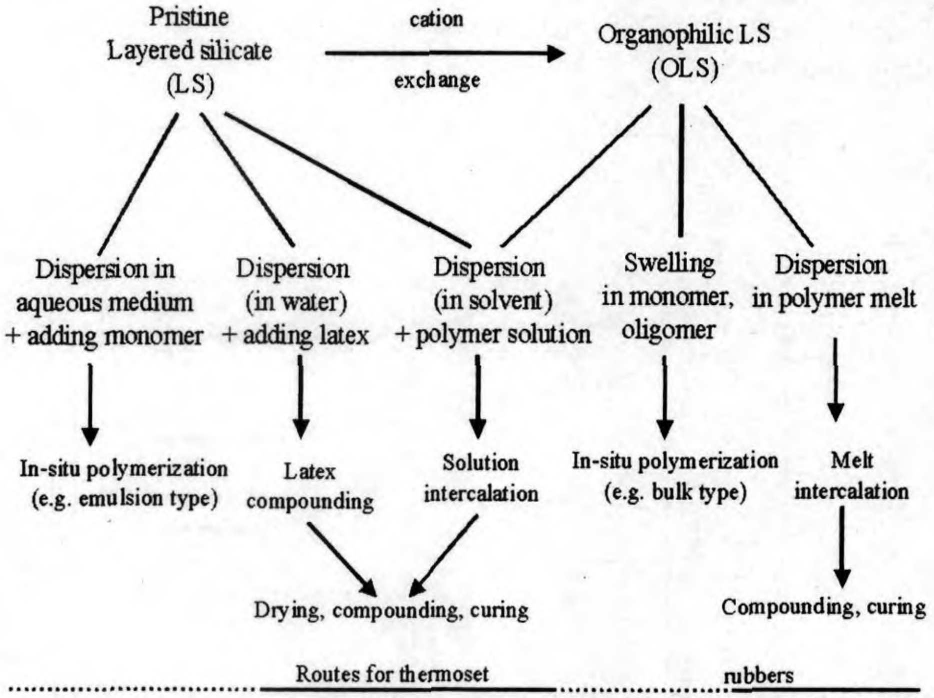
Introduction

Polymeric nanocomposites can be considered as an important category of organic-inorganic hybrid materials in which inorganic nanoscale building blocks (*e.g.* nanoparticles, nanotubes, or nanometer-thick sheets) are dispersed in an organic polymer matrix[1-3]. Improvements in mechanical, thermal and barrier properties, flame retardency etc. are claimed for this class of PLSN that could not be achieved by conventional fillers at such a low loading (typically < 10 phr). Among the different types of layered silicates, layered silicates (LS) are the most widely used materials due their layered structure, very high surface area (700-800 m^2/g), higher cation exchange capacity (90-125 meq/100g clay) and high aspect ratio (100-300).



Scheme 1 : Possible preparation routes of rubber layered silicate Nanocomposites

Experimental

Mixes were prepared in a laboratory model two roll mixing mill. In the case of latex, films were prepared by casting and dried at room temperature and kept for analysis. XRD spectra were obtained in the transmission mode by using Ni-filtered Cu-Kα radiation (λ = 0.1542) by a diffractometer (X' Pert Pro, Panaliticals Ltd, The Netherlands). Transmission electron microscopic (TEM) studies were carried out with a LEO 912 Omega transmission electron microscope with an acceleration voltage of 120 keV. Tensile tests were performed according to the ASTM standard D 412. The DMA measurements were performed on a dynamic mechanical analyzer (DMA-2980, TA Instruments, USA) at a frequency of 10 Hz. Air permeability studies were conducted with circular specimens as per IS: 3400 (part 21)- 1980.

Results and discussion

Figure 1. Shows the X-ray diffraction (XRD) spectra of the LS and the LS-containing films of various compositions. LS has been intercalated by NR in the related compound as the interlayer distance of the LS increased to 1.19-1.31 nm. The appearance of the related broad peak suggests that the degree of NR intercalation is different. A considerably better intercalation was noticed for the polyurethane (PUR) latex where two peaks were resolved. The major peak indicates that the interlayer distance of the LS widened to 1.73 nm from the initial 0.95 nm. This effect can be assigned to the higher polarity of PUR compared to NR which favours the compatibility with LS. Similar to PUR, the NR/PUR latex blend showed two XRD peaks, at slightly higher interlayer distances.

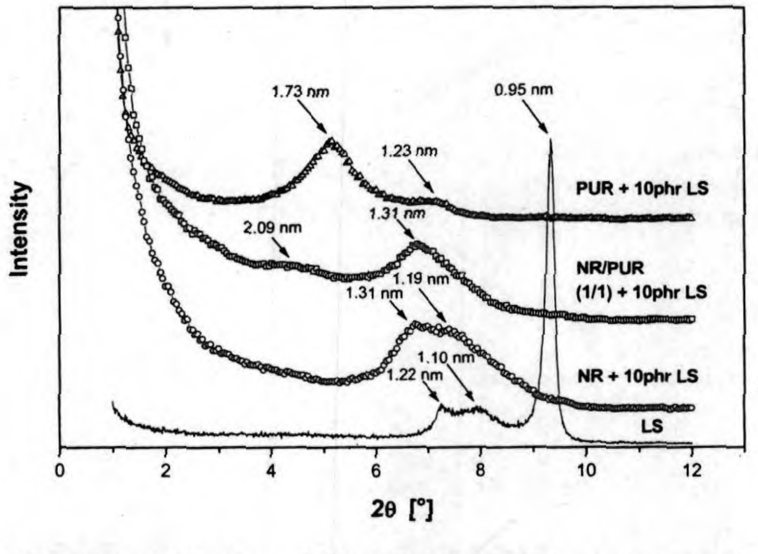


Figure 1 : XRD spectra of the layered silicate reinforced latex nanocomposites of various compositions.

The XRD diffraction pattern of pure MMT and that of the composite (MMT compounded with NR) are given in Figure 2a. It is to be noted that the pure MMT has two peaks (3.45 and 7.45^{o}) which corresponds to an interlayer distances 25.54 and 11.84 A^{o} respectively. When MMT is mixed with NR the above peaks are shifted to lower angles indicating that MMT undergoes very little amount of intercalation with NR. For MMT-DMBT nanocomposite (Figure 2b) these peaks were increased to 32.64 and 15.57 A^{0} respectively. The extent of intercalation is high in MMT-DMBT compared to MMT. In the XRD spectrum of MMT-MDT (Figure not given) an appreciable amount of the clay has been intercalated [3-4].

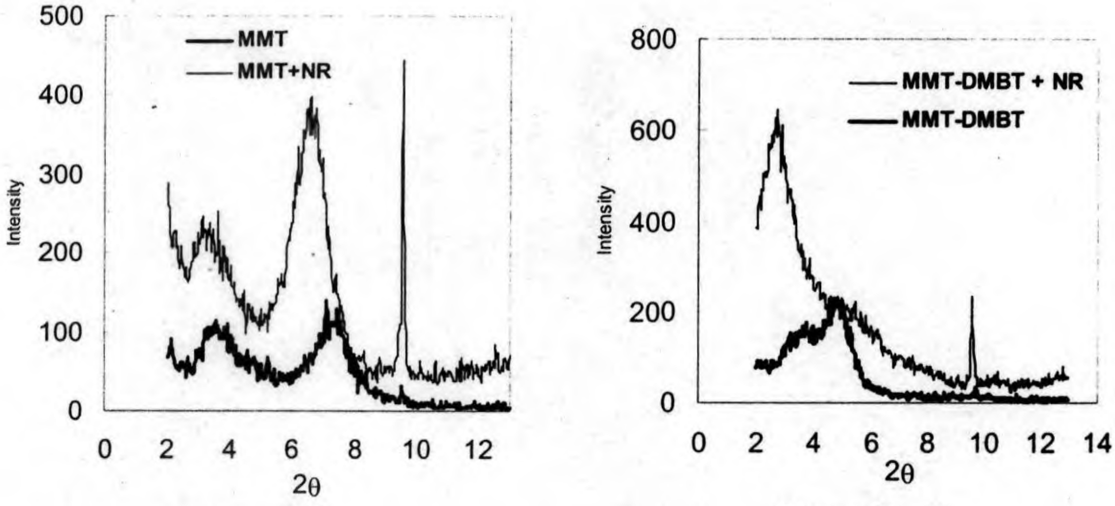


Figure:2a

Figure:2b

Figure 2a : XRD spectrum of pure MMT and that of the NR nanocomposite at 10 phr loading and 2b : XRD spectrum of pure MMT-DMBT and that of the NR nanocomposite at 10 phr loading.

The X-ray diffraction pattern of the MMT-DMDT has two peaks and the corresponding nanocomposites showed three peaks respectively at layer distances. This indicates the contraction of the expanded layers due to the removal of the modifier from the silicate layers which finally leads to lowering of interlayer distance of the clay [4].

The observations from the XRD-data can be further complimented with TEM results. It can be seen that layers of MMT (Figure 3a) remains as agglomerates whereas the layers are intercalated in MMT-DMBT nanocomposite (Figure 3b). However the distribution of silicate layers is not uniform in the matrix.

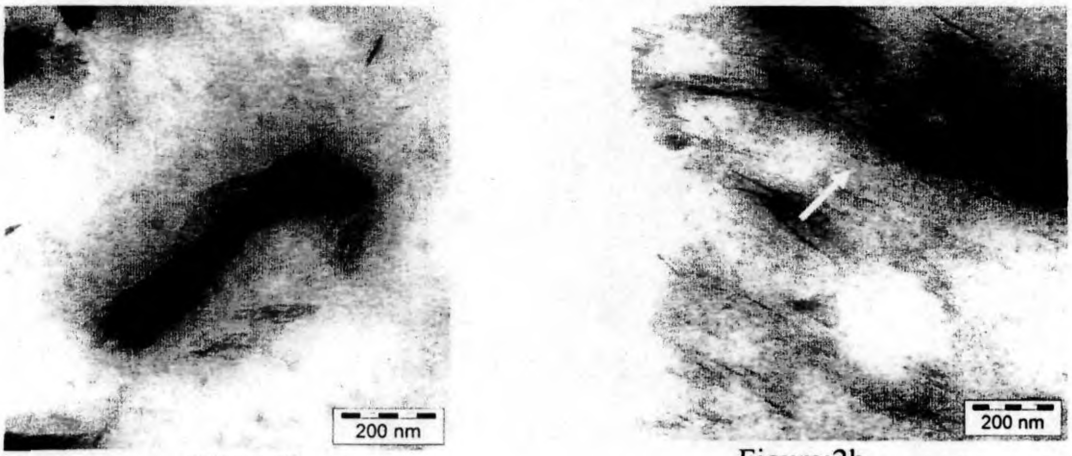


Figure:2a

Figure:2b

Figure 3a : TEM photograph of un-modified MMT incorporated NR nanocomposite 3b : TEM photograph of MMT-DMBT incorporated NR nanocomposite

Figure (1b) compared to the virgin clay (19.2 A^{o}). The TEM photograph of the MMT-MDT is showed that the layers are distributed mainly as single layers more or less in a uniform manner. In the TEM picture of MMT-DMDT the clay layers mainly exist as clusters. As seen in the XRD spectrum, the multiple peaks represent these individual clusters of lower layer distance due to the extraction of modifiers from the layers.

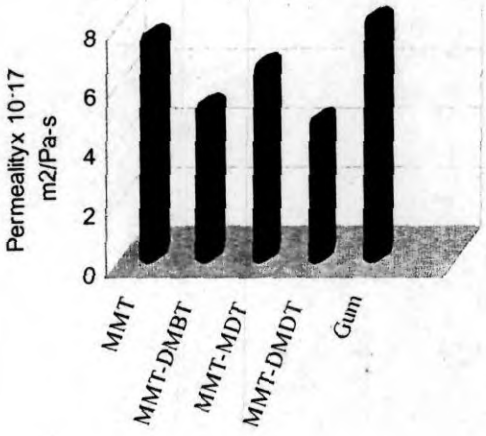


Figure 4 : Air permeability of different nanoclay filled natural rubber nanocomposites

The air permeability of different NR nanocomposites is given in Figure 4. All the composites were loaded with the same amount of clay (10 phr). The control compound (without any filler) showed high air permeability followed by pure MMT. The modified clays *viz* MMT-MDT and MMT-DMBT showed minimum permeability values. The exfoliated silicate sheets contribute to the high impermeability of MMT-MDT and MMT-DMDT significantly.

Fourier transmission infrared spectroscopy (FTIR) can be effectively used for the structure elucidation of PLSN. This is essentially due to the shift in the Si-O stretching (1005 cm^{-1}) and Si-O bending (476 cm^{-1}) vibrations (frequency) to lower wave lengths (Figure 5) due to the interaction of the silicate (intercalation/exfoliation) with the polymer in the composite.

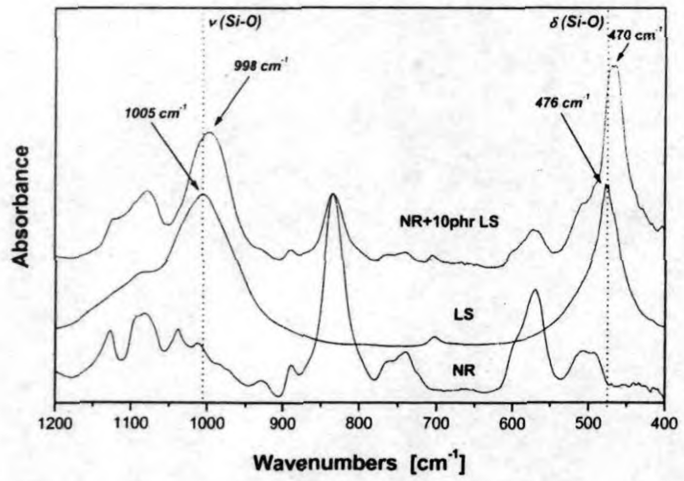


Figure 5 : FTIR spectra of fluorohectorite and NR nanocomposite at 10 phr silicatte loading.

Conclusions

Modifiers of nanoclays being quaternary ammonium compounds influence the amine accelerated vulcanization of natural rubber. Cure acceleration of nanoclays causes extraction of modifiers from clays which leads to lowering of interlayer distance. This lead to poor mechanical, degradation and barrier properties to the NR nanocomposites. Accordingly MMT-MDT is preferred followed by MMT-DMBT for natural rubber nanocomposites. Unmodified MMT being organophobic and having lower interlayer distance leads to poor rubber intercalation and hence is not suitable for dry rubber compounding. XRD, TEM and FTIR techniques can successfully used for the structure elucidation of PLSN.

References

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