Prediction of the forming mechanism of poly(ethylene-oxide)/montmorillonite nanocomposites from nitrogen adsorption isotherms

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Abstract— In this study, we tried to estimate of the formation mechanism of the silica-poly(oxyethylene)-montmorillonite hybrid prepared by the sol–gel route from N_2 adsorption-desorption isotherms. The results revealed that nanocomposites exhibit highly exfoliated dispersion and their porous structure has been almost completely destroyed.

Polymer nanocomposites are a class of hybrid materials composed of an organic polymer matrix with dispersed inorganic nanofillers that have at least one dimension in the nanometer range [1]. Polymer nanocomposites can commonly be obtained by either the sol–gel method or intercalation method. Sol–gel nanocomposites (polymer/silica nanocomposites) are prepared by in situ hydrolysis and condensation of mononuclear precursors such as tetraethoxysilane (TEOS) and tetramethoxysilane in organic polymer matrices [2]. The inorganic clay, used in this study, was K-10 grade montmorillonite purchased from Sigma–Aldrich Co. (USA) with a surface area 220–270 m^2/g. The chemical composition (wt. %) of the clay (main elements) was SiO_2:67.6, Al_2O_3:14.6, Fe_2O_3:2.9, MgO: 1.8 and others. Cation exchange capacity of the clay was 60 meq/100g. Sol-gel nanocomposite (PEO/silica nanocomposites) are prepared by in situ acid catalysed hydrolysis and condensation of mononuclear precursors such as tetraethoxysilane (TEOS) in organic polymer matrices. This procedure was used to prepare the hybrids with TEOS/clay = 20/3 (w/w) and PEO/MMT ratio 10% w/w. The samples characterised using X-ray diffraction (XRD), Fourier Transform Infrared (FT-IR) Spectra. Morphology of the samples was examined by scanning electron microscopy (SEM). It was understood from the results of these characterisation techniques, the near-full exfoliation of MMT on the silica–PEO occurs provided by possible bonding mechanisms such as the H-bonding between water molecules in the hydration sphere of exchangeable cations on montmorillonite and the oxygens of the PEO polymer, and direct ione dipole interactions [3] between the oxygen atoms of PEO and the exchangeable cations [4]. The nitrogen adsorption analysis was performed on an ASAP-2020 instrument at liquid nitrogen temperature. The surface areas and pore size distributions were calculated using the Brunauer–Emmett–Teller and Barrett-Joyner-Halenda (BJH) desorption pore size distributions. The results are given in Table 1.

Table 1. Parameters resulting from the analysis of N_2 adsorption isotherms of clay and poly(ethylene-oxide)/clay–silica nanocomposite.

Sample	BET surface area (m^2g^{-1})	BJH adsorption pore radius (nm)	BJH desorption pore radius (nm)
Clay	279.28	3.1747	2.6296
Nanocomposite	0.6621	35.9608	20.7103

The isotherm of pristine clay (Fig.1) presents a type-H4 hysteresis loop, which can be attributed to mesoporous structure containing open slit-shaped capillaries with wide bodies and narrow short necks. The discrepancy in the average pore sizes between the nitrogen adsorption and desorption (Table 1) is very large because the pore size from adsorption reflects the size of the bottle, and the pore size from desorption is associated with the necks between pores. Pore texture properties of the the pristine MMT and the poly(ethylene oxide)-montmorillonite were determined using the nitrogen adsorption, and desorption isotherms are shown in Fig. 1.

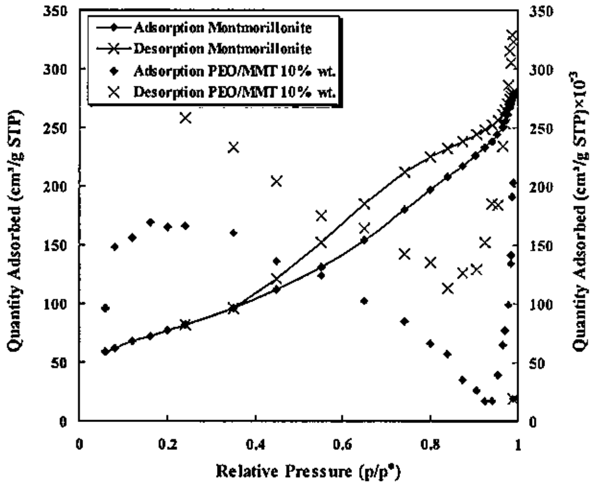

Figure-1: N_2 adsorption–desorption isotherms of the pristine MMT and the poly(ethylene oxide)-montmorillonite

The results in Table 1 and Figure 1 revealed that nanocomposites exhibit highly exfoliated dispersion and their porous structure has been almost completely destroyed. The adsorption and desorption isotherms for the composite in which there is no hysteresis lobe indicates the formation of random pits in the polymer matrix.

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