Dispersion of silicate nano-plates within poly(acrylic acid) and their interfacial interactions

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Abstract

Dispersion of the silicate nano-plates of clays within polymers for nanocomposite formation generally involved interactions of the polymers with the plate surfaces. In this paper, we provide preliminary evidence showing dependency of the dispersion on the interactions of the plate lattices with polymers. Experiments have been carried out on the dispersion of the natural clay, montmorillonite (≈0.5 g) within the aqueous solutions of poly(acrylic acid) at varying temperatures and the products analysed by X-ray diffraction and related techniques. In the product from reaction at 60°C, the silicate plates are dispersed with fully extended chains of poly(acrylic acid) intercalated within the interlayer spaces between unexfoliated plates. Photoemission spectroscopy showed that during the process sodium ions are removed from the silicate surface. In the product from reaction at 85°C or above, the silicate plates are partly exfoliated. During the process, Fe\textsuperscript{2+} ions within the clay lattice are oxidised by the acidic poly(acrylic acid) solution, which suggests strong reaction of poly(acrylic acid) with the silicate plates facilitating exfoliation. Interestingly, the Al and Mg concentrations in the lattice remain virtually unchanged during the reactions.

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1. Introduction

Polymer–clay nanocomposites are formed by the nanoscale dispersion of clay (usually 0.5–5 wt\%) into polymers [1–3]. The small addition of clays leads to remarkable improvements of the mechanical, thermal, optical, physical and chemical properties of the nanocomposites compared to the pure polymers or conventional micro-scale composites. The commonly used clays for formation of nanocomposites consist of nano-plates of silicates (M–O–Si. M: Al, Mg, Fe, etc.). The thickness of the plates is ≈1 nm and the length can be up to 1000 nm or more. The preferential face-to-face stacking of these plates led to formation of regular van der Waals gaps or interlayer spaces, which can trap polymer molecules during the nanocomposite formation.

Formation of polymer–clay nanocomposites, typically exfoliated or intercalated structures, is dependent on the type of dispersion of the silicate plates within the polymer matrix. In particular, intercalated nanocomposites are formed when one or more polymer chains penetrate between the silicate plates; however, the lamellar structures of the clay remain intact. When the plates are completely separated and have random orientation, exfoliated or delaminated nanocomposites are produced. The exfoliated structure is of particular interest because it maximises the polymer–clay interactions (the specific surface area of exfoliated clays is typically 700 m\textsuperscript{2} g\textsuperscript{-1} compared to 2 m\textsuperscript{2} g\textsuperscript{-1} for lamellar clays [4]). Poly(acrylic acid) has polar carboxylic groups and can be used to form block co-polymers (e.g. poly(acrylic acid)–polyurethane), which may further be used for formation of nanocomposites with unique properties [5,6]. Specifically, the poly(acrylic acid)–clay nanocomposites have been used as super-adsorbents of water residues [7]. We have
previously reported the formation of the intercalated poly(acrylic acid)–montmorillonite nanocomposites [8]. In this paper, we examine in more details the polymer–clay dispersion and their interfacial interactions. To this end, the non-destructive, soft X-ray techniques including X-ray photoemission spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) have been used for characterisation of the above products. Soft X-rays have energies lower than $\approx 2000$ eV and can examine elemental environments in clays such as silicon, oxygen, carbon, aluminium and magnesium.

2. Experimental procedure

2.1. Nanocomposite formation

The natural clay montmorillonite with the general molecular structure $\text{M}_x(\text{Al}_{4-x}\text{Mg}_x)\text{Si}_8\text{O}_{20}(\text{OH})_4$ was supplied by Southern Clay Products, Inc. Montmorillonite consists of tactoids or micro-scale particles (average size 13 $\mu$m) formed by stacking of the silicate nano-plates along the $c$-axis or out-of-plane direction. The poly(acrylic acid)–montmorillonite nanocomposites were formed via the exfoliation–adsorption method in which, water was used as a polar solvent for dispersion of montmorillonite into the single silicate plates [1]. In particular, $\approx 0.5$ g of dehydrated montmorillonite was added into 50 g of 5% aqueous solution of poly(acrylic acid) (BDH Chemicals Ltd., MW $\approx$230,000, pH 1.8). The mixtures were stirred between room temperature ($\approx 20$ °C) and 85 °C for 24 h. The product recovered from the reaction at temperatures lower than $\approx 60$ °C appeared as a solid that was easily collected via a centrifuge. In contrast, the product from the reaction at $\approx 85$ °C appeared as a uniform gel.

2.2. Nanocomposite structure characterisation

The low-angle X-ray diffraction (XRD) measurements were carried out using a Philips PW 1825/20 powder diffractometer with a CuK$_\alpha$ source ($\lambda = 1.5418$ Å).

2.3. Polymer–clay interaction

XPS (X-ray photoelectron spectroscopy, electron spectroscopy for chemical analysis) involves the X-ray excitation of photoelectrons from the surfaces and sub-surfaces to the vacuum levels. The energy relationship of the excited photoelectrons is described as follow [9]:

$$E_b = E_{\text{kin}} - h\nu.$$  

(1)

In Eq. (1), $h\nu$ is the total energy used for excitation of the photoelectrons. $E_b$ and $E_{\text{kin}}$ represent the binding energy and kinetic energy of the photoelectrons, respectively. The binding energy values obtained from the measured kinetic energy will provide information concerning the chemical environment of individual atoms. The XPS measurements were carried out using a VG ESCALAB 220i XL photoelectron spectrometer with a monochromated AlK$_\alpha$ source ($h\nu = 1486.6$ eV). Spectra were acquired at the normal incident condition with the photoelectron take-off axis being perpendicular to the sample surface.

NEXAFS (X-ray absorption near-edge structure) involves the transitions of electrons to unoccupied states [10]. A simple example may be the transition of the 1s electrons to the partly empty 2p atomic orbitals in the oxygen molecules. The spectra therefore provide information concerning the atomic environment, which is complementary to the results obtained from XPS. The NEXAFS measurements were carried out at the wide range, bending magnet beamline 24 A (energy $\approx 10$–$1500$ eV), National Synchrotron Radiation Research Centre, Hsinchu, Taiwan [11]. Prior to the measurements, the samples were loaded into a UHV chamber (base pressure $\approx 10^{-8}$ mbar) using a conductive copper tape. The chamber was subsequently heated at $\approx 200$ °C in order to minimise the contamination on the sample surfaces. The fluorescence yield absorption spectra were acquired at normal incident conditions. The resulting spectra were normalised using the standard spectrum recorded from a clean, gold grid reference.

3. Results and discussion

3.1. X-ray diffraction

The XRD experiments were used to measure the interlayer distances formed by the nano-silicate plates within montmorillonite. The XRD patterns of montmorillonite reference and the products recovered from the reactions between montmorillonite and poly(acrylic acid) at varying temperatures are shown in Fig. 1. The main peak in the diffraction pattern of montmorillonite (2θ $\approx 6.9$) was attributed to the formation of the interlayer spaces by regular stacking of the silicate layers along the $c$-axis or out-of-plane direction. The interlayer distance estimated from the 20 value was 13 Å. The out-of-plane peak for the solid product recovered from the reaction between poly(acrylic acid) and montmorillonite at 60 °C was detected at 2θ $\approx 4.7$, corresponding to an increase of the interlayer distance to 20 Å. The increases in interlayer distance were due to the segregation and adsorption of the poly(acrylic acid) molecules into the interlayer spaces leading to formation of intercalated nanocomposites. Our previous experiments have shown that the poly(acrylic acid) chains also intercalated within the interlayer spaces at temperatures of 20 and 30 °C [8]. In particular, the XRD results of the products recovered from the reactions at these temperatures indicated that the interlayer spaces slightly decreased compared to those of the product at 60 °C. This suggested that increasing the temperatures facilitated more poly(acrylic acid) chains being intercalated within the interlayer spaces. The diffraction pattern of the gel product recovered from the reaction at $\approx 85$ °C was not well-defined compared to that of the solid products at lower than 60 °C. In this case, the observed gel form (rather
than the solid form) combined with the XRD results suggested that the reaction at \( \approx 85 \, ^\circ \text{C} \) resulted in a greater distribution of the silicate plates within the polymer matrix. The gel may be defined as partially exfoliated nanocomposites, which contained both intercalated and exfoliated silicate plates. In order to understand in more details the varying dispersion of silicate plates within poly(acrylic acid), we employed the element-specific, soft X-ray-based techniques.

### 3.2. X-ray photoemission spectroscopy

Fig. 2 shows the XPS wide scans of the montmorillonite reference standard and the nanocomposites prepared at varying temperatures. In the wide scan of montmorillonite, the main peak from the O 1s photoelectrons was attributed to the Si–O–M (M: Mg, Al, Fe, etc.) components within the lattice of silicate plates. The peaks of Si 2p (or Si 2s) and Al 2p (or Al 2s) photoelectrons were due to the presence of Si–O–Al as major components of the silicate plates [12]. The peaks for Fe 2p (or Fe 3p) and auger Mg KLL (or Mg 2s, Mg 2p) photoelectrons were attributed to the minor Si–O–Mg and Si–O–Fe components (substitutions between Fe\(^{2+}\), Al\(^{3+}\), and Mg\(^{2+}\) ions generate negatively charged silicate layers, which are balanced by the adsorption of Na\(^+\) ions). The peak of Na 1s (or auger Na KLL) photoelectrons was due to the sodium ions on the silicate surface.

In the XPS wide scan of the nanocomposites prepared at 60 and 85 °C, the C 1s peak was assigned as due to the presence of poly(acrylic acid). Other peaks such as Si 2p, Al 2p and Fe 2p were due to the presence of montmorillonite. The O 1s peak was due to both montmorillonite and poly(acrylic acid). The Na 1s and Na KLL peaks were, however, not detected in the wide scan of the nanocomposites. These results indicated that sodium ions have been removed from the silicate surface during the poly(acrylic acid) montmorillonite reactions. They are probably replaced by protons from the poly(acrylic acid) solution [8]. In support of this, our experiments with synthetic phyllosilicate clays showed the increased concentration of the silanol groups –SiOH on the plate surface after poly(acrylic acid) intercalation [13].

A more detailed analysis of the XPS results was carried out using the high-resolution region scans. Fig. 3 shows the C 1s region scans for the poly(acrylic acid) standard and the nanocomposites prepared at varying temperatures. In the scan of poly(acrylic acid), the binding energy of C 1s
photoelectrons from the C–C and C–COOH species was measured at $E_b = 285.0$ and 289.1 eV, respectively [14,15]. The shoulder within the energy range of 286.0–287.5 eV has been assigned as due to the presence of the C–OH or C–O–C species, probably related to the molecular rearrangements induced by the monochromated X-ray source [14,16]. The C 1s region scans of the poly(acrylic acid)–montmorillonite nanocomposites were similar to that of the poly(acrylic acid) standard. The combined results show that the poly(acrylic acid) molecules have chemically exchanged sodium ions on the silicate surface of montmorillonite.

In the O 1s scan of poly(acrylic acid) (Fig. 4), the peaks at $E_b = 532.2$ and 533.3 eV were attributed to the presence of the carbonyl and hydroxyl species of the carboxylic group [15]. The O 1s peak in the scan of montmorillonite ($E_b = 532.0$ eV) was attributed to the presence of oxide O–M (M: Si, Al, Fe and Mg) [12]. In comparison, the main peak from the O 1s scans of the intercalated/partially exfoliated nanocomposites ($E_b = 532.1$ eV) was due to the carbonyl and oxide species from poly(acrylic acid) and montmorillonite, respectively. In addition, the shoulder at higher binding energy ($E_b = 533.3$ eV) was due to the hydroxyl species from the carboxylic group. The relatively broader O 1s peak from the nanocomposite prepared at 85°C, compared to that from the 60°C nanocomposite, was probably due to greater polymer–clay interactions.

### 3.3. Near-edge X-ray absorption fine structure

Fig. 5 shows the Fe $L_{3,2}$ edge NEXAFS fluorescence yield spectra of montmorillonite and nanocomposites prepared at temperatures lower than $\approx 85\, ^\circ\mathrm{C}$. These spectra were probably related to the electronic transitions of the 2p electrons to the partly empty 3d orbitals of Fe.

The main, Fe $L_3$ edge peak of the NEXAFS spectrum of montmorillonite ($\approx 708.0$ eV) was attributed to the presence of Fe$^{2+}$ ions [17–20]. The shoulder at the higher energy ($\approx 711.0$ eV) was attributed to Fe$^{3+}$ ions. Of significance is the energy shift of the main peak in the Fe $L_{3,2}$ edge NEXAFS spectrum of the exfoliated nanocomposites to the higher energy sites. This was interpreted as due to co-ordination of Fe$^{2+}$ ions by poly(acrylic acid) and suggests that formation of the exfoliated structure involves the strong chemical absorption of poly(acrylic acid) molecules into the lattice (bulk) of silicate plates.

Fig. 6 shows the Al $K$ edge NEXAFS fluorescence yield spectra of montmorillonite and the nanocomposites prepared at temperatures lower than $85\, ^\circ\mathrm{C}$. These spectra are probably due to the electronic transitions between the 1s orbitals and the partly empty 3p states of Al. They
predominantly reflected the presence of the octahedrally co-ordinated structures of Al atoms within montmorillonite. The NEXAFS results were in reasonable agreements with those from kaolinite clays [21] (the Al K edge NEXAFS spectra were dependent on the relative concentration of aluminium within clays [22]). In particular, the shapes of the Al K edge spectra in montmorillonite and nanocomposites remained virtually unchanged, which suggested that the aluminium ions were not involved in the reactions leading to the intercalated/exfoliated structures. Similar results were also obtained from the Mg K edge NEXAFS spectra of these nanocomposites.

The schematic in Fig. 7 shows the proposed model of the dispersion of silicate plates within the polymer matrix. In particular, Fig. 7A shows the ideally intercalated structures. In Fig. 7B, small groups of silicate plates were distributed randomly, which eventually resulted in the formation of uniform gel or partially exfoliated structures. Similar results were also obtained from the Mg K edge NEXAFS spectra of these nanocomposites.

Fig. 6. Al K near-edge X-ray absorption fine structure spectra of: (a) dehydrated montmorillonite; (b) intercalated nanocomposites and; (c) partially exfoliated nanocomposites.

Fig. 7. Schematic showing the structures of: (A) fully intercalated nanocomposites and (B) partially exfoliated nanocomposites.

combined results implied that the nano-scale dimension and chemistry of the silicate plates greatly influence the dispersion of the plates within polymers.

4. Summary

The dependency of the silicate dispersion on the interfacial interactions within poly(acrylic acid)–clay nanocomposites has been observed. Dispersion of the silicate plates within the polymer at temperatures lower than 60 °C resulted in the formation of a solid product which is an intercalated nanocomposite. Photoemission spectroscopy shows that the poly(acrylic acid) molecules have facilitated loss of sodium ions from the silicate surface of montmorillonite. A greater dispersion of the silicate plates at temperatures >85 °C resulted in a uniform gel, which is a partially exfoliated nanocomposite. NEXAFS shows oxidation of Fe2+ ions by the acidic poly(acrylic acid) solution, showing that chemical interactions of poly(acrylic acid) with the lattice (bulk) of silicate facilitated the increased dispersion.

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References

[1] M. Alexandre, P. Dubois, Mater. Sci. Eng. 28 (2000) 1-63.
[2] S.S. Ray, M. Okamoto, Prog. Polym. Sci. 28 (2003) 1539–1641.
[3] T.J. Pinnavaia, G.W. Beull, Polymer-clay nanocomposites, Wiley Ser. Polym. Sci. (2000).
[4] H.J. Ploehn, C. Liu, Ind. Eng. Chem. Res., ASAP article, available online, 2006.
[5] S.H. Back, B.S. Kim, B.K. Kim, Prog. Org. Coat. 49 (2004) 353.
[6] S. Saimani, K. Tharanikkarasu, G. Radhakrishnan, J. Appl. Polym. Sci. 87 (2003) 1109.
[7] J. Lin, J. Wu, Z. Yang, M. Pu, Macromol. Rapid Commun. 22 (2001) 422-424.
[8] N.H. Tran, G.R. Dennis, A.S. Miley, G.S.K. Kannangara, M.A. Wilson, R.N. Lamb, J. Colloid Interface Sci. 290 (2005) 392.
[9] D. Briggs, M.P. Seah, Practical Surface Analysis, Vol. 1: Auger and X-ray Photoelectron Spectroscopy, Wiley, Chichester, 1990.
[10] A. Bianconi, A. Marecelli, Synchrotron radiation research, in: R.Z. Bachrach (Ed.), Advances in Surface and Interface Science and Refs therein, vol. 1, Plenum Press, New York, 1992, p. 63.
[11] J.L. Lai, P.C. Tseng, Y.W. Yang, S.C. Chung, Y.F. Song, N.F. Cheng, C.C. Chen, C.T. Chen, K.L. Tsang, Nucl. Instr. Methods Phys. Res. A 586 (2001) 467–468.
[12] H. Seyama, M. Soma, J. Chem. Soc. Faraday Trans. I 81 (1985) 485.
[13] N.H. Tran, M.A. Wilson, G.R. Dennis, A.S. Miley, G.S.K. Kannangara, A.L. McCutcheon, R.N. Lamb, Langmuir 22 (15) (2006) 6696.
[14] L.J. Ward, W.C.E. Schofield, J.P.S. Badyal, Chem. Mater. 15 (2003) 1466.
[15] G. Beamson, D. Briggs, High-Resolution XPS of Organic Polymers: The Scienta ESCA300 Database, first ed., Wiley, Chichester, 1992.
[16] S.R. Leadley, J.F. Watts, J. Electron. Spectrosc. Relat. Phenom. 85 (1997) 107.
[17] L.A.J. Garvie, P.R. Buseck, Nature 396 (1998) 667–670.
[18] S. Sun, S. Anders, H.F. Hamann, J.U. Thiele, J.E.E. Baglin, T. Thomson, E.E. Fullerton, C.B. Murray, B.D. Terris, J. Am. Chem. Soc. 124 (12) (2002) 2884–2885.
[19] A.D. Smith, G. Cressey, P.F. Schofield, B.A. Cressey, J. Synchrotron Radiat. 5 (1998) 1108–1110.
[20] C.S. Chan, G.D. Stasio, S.A. Welch, M. Girasole, B.H. Frazer, M.V. Nesterova, S. Fakra, J.F. Banfield, Science 303 (2004) 1656–1658.
[21] M. Gehlen, L. Beck, G. Calas, A. –M. Flank, A.J. Van Bennekom, J.E.E. Van Beusekom, Geochem. Cosmochim. Acta 66 (9) (2002) 1601–1609.
[22] Y. Kato, K. Shimizu, N. Matsushita, T. Yoshida, H. Yoshida, A. Satsuma, T. Hattori, Phys. Chem. Chem. Phys. 3 (2001) 1925–1929.