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Preparation and Characterisation of Li-Al-glycine Layered Double Hydroxides (LDHs)-Polymer Nanocomposites

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Summary: LiAl-Layered Double Hydroxides, containing glycinate anions, have been prepared using $LiAlO_2$. The glycine containing LDHs were then exfoliated in chloroform. Dispersions of approximately 0.03 g of the LDH in 15 ml of the solvent were possible. Nanocomposites using the exfoliated LiAl-glycine LDH and polyethyleneglycol were prepared by adding appropriate amounts of polymer to the LDH-chloroform dispersion. The clay-polymer nanocomposites were then characterised using powder X-ray diffraction. The thermal and mechanical properties of the composites are reported. The results suggest that composites containing individual (exfoliated) LDH layers were obtained with the mechanical and thermal properties of the composites noticeably superior to those of the parent polymer.

Keywords: dispersion; exfoliation; layered double hydroxides; nanocomposites; polymer

Introduction

Nanocomposites consisting of the assembly of a lamellar nano-sized inorganic host structure (eg silicates) dispersed within a polymer have gained considerable importance [1]. Early work on the development of polymer – cationic clay (silicate) nanocomposites (e.g. with montmorillonite and hectorite clays) for materials applications can be traced to the late 1980s and the work on polyamide – clay nanocomposites of the Toyota group [2].The Toyota nanocomposites were found to possess properties superior to those of conventional composites, primarily, it is believed, because interfacial adhesion between the clay surface and the polymer was maximised. Improved features for the nanocomposites include mechanical properties (such as modulus, strength, heat distortion temperature, thermal expansion co-efficient), enhanced barrier properties, thermal stability, resistance to solvent swelling, flammability resistance, and ablation performances compared to unmodified

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polymers and conventional composites.[3-6] It is noteworthy that these improvements were achieved with less than 10% addition of the inorganic material to the overall composite.

From a structural viewpoint, polymer-clay nanocomposites may be broadly classified into two types: (1) intercalated nanocomposites, where either one or a small number of molecular layers of polymer are intercalated into the galleries of the layered material and (2) exfoliated nanocomposites, where the individual layers of the layered compound are dispersed within the polymer matrix[3].

There are three general approaches to the preparation of clay-based nanocomposites. (1) Intercalation of the monomer molecules followed by *in situ* polymerisation; the product may be an intercalated or an exfoliated nanocomposite. (2) Direct intercalation of polymer chains into the host lattice. (3) Transformation of the host material into a colloidal system followed by refoliation in the presence of the polymer.

Layered double hydroxides (LDHs) are another class of layered materials, which are suitable for preparation of nanocomposites.[7] An alternative name frequently used for these materials is anionic clays, reflecting the complementary to the cationic clay family. LDHs present a large variety of compositions and tunable layer charge density [8, 9]. They can easily be synthesised in a relatively pure form under ambient conditions and at low cost.

The use of LDHs in nanocomposite formation has been recently reviewed [7]. Various methods are available for the preparation of LDH-polymer intercalated nanocomposites[3 10-14]. The preparation of exfoliated nanocomposites via transformation of the host lattice into a colloidal system followed by refoliation in the presence of a polymer[15-17] has, however, received less attention due to the difficulties that arise in the exfoliation of LDHs. [18, 19]

In the present contribution, we describe the preparation of LDH/polymer nanocomposites via exfoliation of a Li-Al-glycine LDH in chloroform followed by refoliation in the presence of polyethyleneglycol (PEG). The results from this study suggest that the exfoliated LDH layers are well dispersed within the polymer matrix. In addition, we report a significant improvement in the thermal and mechanical properties of the nanocomposite compared to the parent polymer.

Experimental

Synthesis of LiAl-glycine LDH

0.1 g of $LiAlO_2$ was stirred with 50 ml of a 2 M sodium glycinate solution for 3 days at room temperature under an Ar atmosphere. The resulting slurry was filtered and washed with de-ionised water and dried at room temperature.

Exfoliation of LiAlglycine LDH

0.03 g of the glycine LDH was dispersed in 15 ml chloroform and stirred at room temperature until a clear solution was obtained.

Preparation of LDH-polymer nanocomposite

Appropriate amounts of polyethyleneglycol (MW 10000, white flakes) were added to the LDH – chloroform dispersion (0.03g of LDH in 15 ml of chloroform) and stirred for three days at room temperature. The solvent was then evaporated quickly at 65 °C in order to avoid aggregation of the LDH platelets and the resulting solid was characterised by powder x-ray diffraction (PXRD) and mechanical and thermal properties measured. The composites contained 98, 95 and 90 wt% polymer.

Results and Discussion

PXRD patterns for the parent glycine LDH, the exfoliated and the redeposited product and the nanocomposites prepared with different amounts of clay loading are shown in Figure 1. The first reflection of the glycine LDH suggests an interlayer repeat distance of 12.40 Å. Taking into account that the thickness of the layer is 4.8 Å, a gallery height of 7.6 Å is suggested. An interlayer repeat of 12.40 Å is considerably higher than the value of 8.1 Å reported by Hibino and Jones for a MgAl-glycine LDH [20]. Since the length of the glycine anion is approximately 3.9 Å, the most likely arrangement of anions in the LiAl-glycine LDH is as a bilayer of glycinate anions. The reflections around 11.8 and 23.54 °2θ may be due to a second LDH phase and the corresponding interlayer spacing for this phase is 7.5Å. The crystalline impurities may be unreacted $LiAlO_2$ (ICSD number 38-1464), gibbsite (ICSD number 01-0263) and Li glycine salt. However, it is not possible to unambiguously assign phases to the extra reflections since there are some reflections common for all three impurity phases. None of the impurities were removed by repeated washing with deionised water.

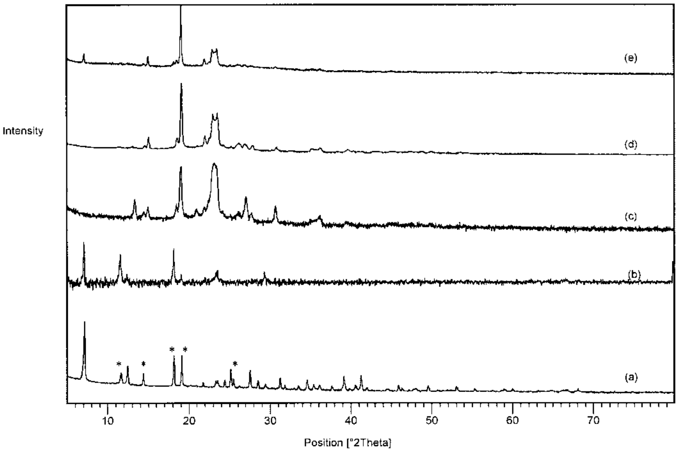

Figure 1. Powder X-Ray patterns for (a) parent LiAlglycine LDH, (b) LDH resulted after exfoliation and redeposition of glycine LDH, (c) polyethyleneglycol, (d) nanocomposite with 5% LDH loading, and (e) nanocomposite with 10 % LDH loading nanocomposite (* Li glycine salt impurities).

The formation of nanocomposites with exfoliated clay materials (with 2% and 5% LDH loading) is suggested principally by the absence of basal reflections associated with the LDH. The absence of the (00l) reflection is, however, not a direct evidence of the formation of an exfoliated LDH–polymer nanocomposite because for a 2% clay loading is likely to under the minimum detection limit for PXRD and at 5% clay will be very close to the minimum. The presence of (00l) reflections in the nanocomposite with 10 % LDH loading (Figure 1(e)) indicates some ordering of the LDH material within the polymer matrix for this material. However, the interlayer spacing of the LDH is similar to that of the original glycine LDH suggesting that the product is not a mixture of polymer intercalated and exfoliated nanocomposites. Instead it is likely that tactoids of the original inorganic material are present within the matrix together with exfoliated layered material.

Figure 2 indicates the thermogravimetric curves of the polymer and the 10 wr% LDH-polymer composite.

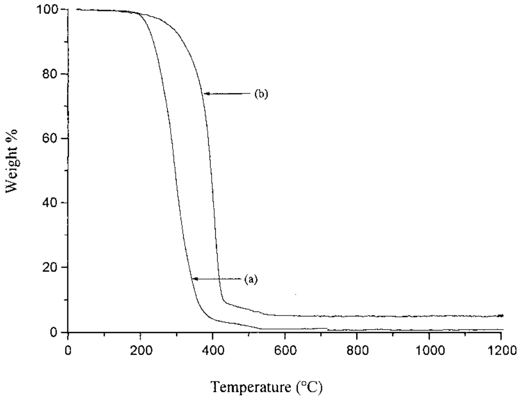

Figure 2. TGA curves of (a) polyethyleneglycol, (b) nanocomposite with 10% LDH loading.

Three weight losses are observed for the parent polymer and the nanocomposite. The first (minor) weight loss (up to *ca* 200 °C), corresponds to elimination of water, the second to (*ca* 400 °C) dehydroxylation and partial decomposition of the polymer and the final step (> 400 °C) to oxidative elimination of the carbonaceous residue derived from the initial polymer degradation[13]. There is a clear increase in the temperature regions for weight loss after addition of the LDH (approximately 100 °C). A factor leading to the increased stability will be the well dispersed inorganic material acting as a gas barrier, preventing evolution of volatile gases from the thermally decomposed products [11].

Table 1 summarises the maximum load and the tensile strength values of the composite materials with 2 and 5wt% loadings.

Table 1. Mechanical properties of the nanocomposites.

Sample	Area of the fracture (mm^2)	Maximum force (N)	Tensile strength (N/mm^2)
Polyethyleneglycol	9.2	0.40	0.04
Nanocomposite with 2% LDH	2.30	0.42	0.18
Nanocomposite with 5% LDH	5.10	0.64	0.12

The data clearly shows that the LDH-polymer nanocomposites are mechanically more stable than the parent polymer. The maximum tensile strength was observed with 2% LDH loading, with a value 45% higher than that of the parent polymer.

Conclusions

We have demonstrated that LiAl LDHs can be readily prepared from $LiAlO_2$ as the starting material. Exfoliated LiAlglycine LDHs were used to prepare LDH-polyethyleneglycol nanocomposites. XRD measurements indicate that the individual LDH platelets are well dispersed within the polymer matrix up to 5% LDH loading. The presence of exfoliated LDH platelets within the polymer matrix improves the mechanical and thermal properties of the parent LDH.

In preparation of nanocomposites it is important to consider the compatibility between the polymer material and the LDH because lack of adhesion between the two compounds may lead to phase separation[11]. The amino groups of the glycinate anion interacts with the hydroxyl groups of the polymer through H-bonding in order to generate adhesion between the LDH and polymer making the exfoliated LDH and the polymer more compatible leading to LDH – polymer with dramatically improved mechanical and thermal properties over those of the parent polymer. TEM/SEM investigations are currently under way as well as FTIR and Raman spectroscopy. The use of other polymer matrices will also be presented.

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