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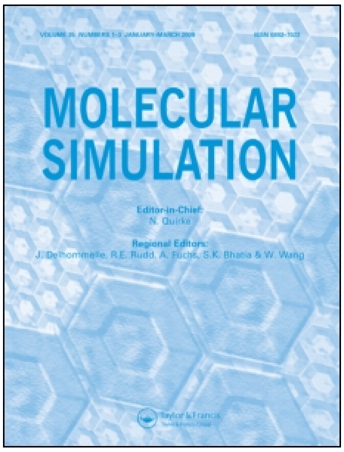

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NOVEL NON-EXFOLIATED CLAY-NANOCOMPOSITE MATERIALS BY *IN SITU* CO-POLYMERISATION OF INTERCALATED MONOMERS: A COMBINATORIAL DISCOVERY APPROACH

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We report the synthesis and qualitative testing of a novel class of clay nanocomposite materials made by the *in situ* copolymerisation of small intercalating monomer molecules using combinatorial-style diversity methods. Initial screening was undertaken by treating montmorillonite clay films with combinations of selected additives in aqueous solution. The treated films were assessed for their stability in a qualitative manner based on their response to water. The mechanical strength of these films was also assessed qualitatively. Promising "lead" formulations showed no signs of water-induced swelling and/or exfoliation, while also being flexible and hard. In addition, the interlamellar *d*-spacings in the treated clay films were measured using X-ray diffraction, where possible; the value of the *d*-spacing in the treated clays was found to vary significantly, from 12.7–17.7 Å. The lead formulations were then tested on bulk montmorillonite clay, confirming that the thin film behaviour was representative of that of the bulk. Direct analysis of the treated clays by mass spectrometry using both FAB and MALDI-TOF did not provide any useful information. However, when the clays were subjected to extraction using chloroform, clear evidence of higher relative molecular mass species was forthcoming, confirming that polymerisation of the additives was occurring. Further supporting evidence was obtained by solid-state NMR analysis of treated iron-free (laponite) clay samples, which also revealed extensive polymerisation of the monomers used. Comparison of these data with the results of some simple molecular modelling studies indicates that polymerisation is indeed occurring within the clay galleries.

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Keywords: Clay; Nanocomposites; Combinatorial discovery

1. INTRODUCTION

The discovery that polymers can enter clay galleries, either expanding the basal inter-planar spacing or causing exfoliation, has opened up a new class of polymer-clay nano-composites, also called intercalated clay composites. The reinforcing aluminosilicate layers in these materials are small ($< 1\mu m$) but the platelet aspect ratios are high (200 – 2000) and, as a result, significant property enhancement has been realised.

The quest for tough, high modulus polymer composites continues. *Abalone* (mother of pearl) is frequently cited as the structure to be emulated either by innovative processing or by *in vitro* biomineralisation [1]. Similar structures, consisting of mineral platelets separated by thin polymer layers, can now be achieved by intercalation. These consist either of thermosetting matrix systems in which oligomers enter the clay galleries and polymerise *in situ* [2] or thermoplastic matrix systems in which polymer molecules diffuse in the melt between the weakly bonded layers. This provides a composite material that consists of alternating thin layers of polymer between aluminosilicate monolayers [3, 4]. The high aspect ratio of clay layers provides reinforcement comparable to that of fibres [2]. Incorporation of 5% montmorillonite in nylon 6 provides an increased fracture strength and modulus, as well as reduced gas permeability.

Three types of composite can be distinguished by observing the integrated intensity of the X-ray reflection from the basal plane of the aluminosilicate host. In a conventional composite, aggregated clay tactoids remain bonded giving a low aspect ratio particle filled polymer. In intercalated composites, the regular insertion of polymer layers in the host galleries provides a layered structure with nanometre-wide organic layers. In exfoliated composites, aluminosilicate monolayers are dispersed but disordered, allowing for a lower mineral volume fraction.

Originally, work was focused on nylon-montmorillonite composites at Toyota Research Labs [5, 6]. Thermoplastics that have been intercalated include polystyrene, polyvinyl pyridine, polyethylene oxide, polysiloxanes, polyamides and polyesters [7]. The rate of migration into the galleries shows similar molecular weight dependence and self diffusion coefficient to the bulk [7]. Nylon 6-clay hybrids are already used in automotive parts [8]. That the matrix material may be chosen very widely is confirmed by the use of non-polar polymers such as polypropylene which have been intercalated into fluorinated mica and montmorillonite after pretreatment of the mineral with stearylamine [9].

As an alternative to the adsorption of polymers into the clay matrix, lower molecular weight organic molecules can displace water from the galleries and subsequently may then be polymerised *in situ* to produce exfoliated materials. This method is ideal for preparing compounds which are strong and insoluble in water, particularly using epoxy compounds yielding an exfoliated material (Fig. 1) [10, 11]. It is of considerable interest to achieve *in situ* polymer formation through crosslinking with minimal or zero exfoliation since the composites derived would retain the sandwich like morphology of the clay, inter-spaced with polymer, conferring mechanical strength coupled with minimal attendant volume increase. The present paper describes work aimed at achieving exactly this, that is clay intercalation and copolymerisation, under mild conditions and with little attendant exfoliation, while profoundly changing the physical properties (see Tab. I below). There is evidently scope for developing new nanocomposite materials for a wide range of novel applications in which the clay content is high and the polymer content low, and it is this philosophy which underpins the current work.

Given the wide range of possible materials properties emergent from our approach, we decided to use a combinatorial diversity method [12] to assess the range of additives and chemical treatments that could potentially be useful for forming such clay-nanocomposites. In order to do this, it was necessary to develop small scale, parallel combinatorial methods which allowed rapid, simple testing and analysis of combinations of monomer formulations. Our procedure was to take small films of Wyoming montmorillonite, treat them with a combination of reagents which might be capable of cross-linking and/or polymerising inside the clay layers and then examine the resulting clay for any indications of exfoliation, strength, and rigidity. It should be emphasised that to date we have only done materials property evaluation in a qualitative manner, but hope to return in the future with a more detailed study of materials processing and testing.

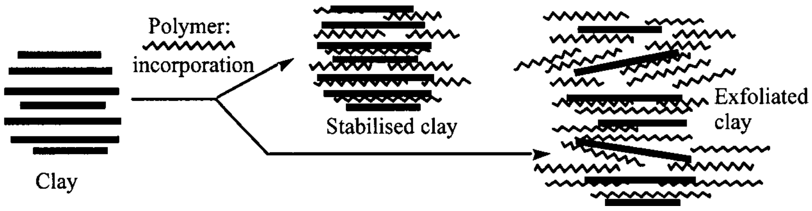

FIGURE 1 Diagramatic representation of the effect of *in situ* epoxy resin Formation on clays.

TABLE I Selected clay-nanocomposite films. The additive combinations listed in Formulations 2 and 3 provided particularly impressive film properties, in terms of enhanced mechanical strength and stability in water, Formulations 14 and 15 were of moderate stability, while 12 and 16 gave very poor properties. (na- no adjustment of solution pH was made)

Formulat