

SYNTHESIS OF THERMOPLASTIC/THERMOSET HYBRID SYSTEMS FOR THE PREPARATION OF CLAY NANOCOMPOSITES BASED ON UNSATURATED POLYESTER RESINS

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Keywords: Unsaturated polyester resin, Clay nanocomposite, Thermoplastic/thermoset hybrid, in-situ polymerization

Abstract

In situ copolymerization of methyl methacrylate/styrene P(MMA/S), in the presence of Cloisite 20A, was used to prepare thermoplastic/thermoset hybrid systems to improve different properties of clay nanocomposites based on unsaturated polyester resins. This approach provided an improvement in the degree of dispersion and delamination of the silicate layers as well as synthesis a thermoplastic component in the system. X-ray diffraction and transmission electron microscopy (TEM) revealed a fine intercalation/exfoliation structure in the nanocomposites. The morphology study showed a particulate structure for hybrid systems in which spherical domains of thermoplastic-rich phase containing clay dispersed in the thermoset matrix. As a result, the combination of clay and thermoplastic resulted in a synergistic improvement in the fracture toughness.

1 Introduction

Unsaturated polyester resin (UPR), containing unsaturated polyester molecules (UP) and styrene as a diluent, is a thermoset polymer widely used in composite applications due to its low cost, versatility, excellent wetting and ease of curing. However, its high volume shrinkage and brittleness call for the use of reinforcements and additives in many applications [1]. Since nano-reinforced matrix materials can lead to improved composite products, the preparation of UPR based nanocomposites has attracted a lot of interest. Montmorillonite (MMT), a mica type silicate with a layered structure, has been commonly employed as a nano-reinforcement because of the high aspect ratio of its crystal layers (10-2000)[2]. The preparation of clay nanocomposites based on thermoset resins, such as vinyl ester, and UPR, includes swelling and dispersing of organoclay in the matrix, followed by network formation during curing. In resin systems composed of two or more components with different molecular sizes, as UPR, simple mechanical mixing of the clay and resin leads to a high concentration of styrene inside the clay galleries as a result of the high diffusion rate of styrene as compared to that of the long polyester molecules. A reduction in the degree of cure and total crosslinking density occurs due to the lack of curing agent in the extragallery regions. To avoid the accumulation of styrene monomers inside the galleries, Suh *et.al* [3], proposed a sequential mixing method consisting of preparation a mixture of the clay and the thermoset prepolymer (without styrene) followed by mixing with the reactive diluents. They claimed that this mixing method led to homogenous dispersion of styrene monomers and

polyester molecules inside and outside of the galleries providing data showing higher crosslinking density. However, none of the poor properties of UPR such as brittleness and shrinkage were evaluated in their study. In general, in the literature, nanoclay has been mostly useful to partially improve certain mechanical properties while shrinkage control and fracture toughness have not been significantly improved by the addition of clay. In our work, we address the fracture toughness property by combining well-dispersed clay in a hybrid thermoplastic/thermoset system. In fact, an incompatible thermoplastic additive in thermoset systems forms a dispersed particulate phase which could result in an improvement in the fracture toughness [4,5].

In the present work, in situ copolymerization of methyl methacrylate (MMA) and styrene (St) in the presence of clay is used to improve the dispersion and delamination of the silicate layers and also to synthesize a thermoplastic additive. MMA also acts during curing to promote styrene conversion, the reactions inside clay galleries, as well as reactions in the thermoplastic-rich phase by MMA/St copolymerization.

2 Experimental

2.1 Materials

Cloisite 20A (Southern clay products Inc.) was used as the nanoclay. Methyl methacrylate and styrene (Sigma Aldrich) were distilled prior using an IKA rotary evaporator under vacuum at 30 °C to remove the inhibitors. Benzoyl peroxide (Sigma Aldrich) was used as a thermal initiator for the thermoplastic synthesis and the room temperature initiator employed for curing the whole system was methyl ethyl ketone peroxide (NOROX, MEKP-925H from NORAC Inc.). The unsaturated polyester resin (H596-CWA-12, Ashland chemical), is a general purpose orthophthalic resin synthesized from maleic anhydride, phthalic anhydride, and propylene glycol. It contains 45wt% of styrene and 0.1wt% cobalt octoate promoter.

In this work we consider 3 different classes of materials: (1) simple polyesters (SP) which contain unsaturated polyester and one or two crosslinking agents; (2) simple nanocomposites (SN) which contain Cloisite 20A in addition to the components of class 1; (3) hybrid nanocomposites (HN) which contain the thermoplastic additive (copolymer of methyl methacrylate and styrene) in addition to the components of class 2.

2.2 In situ polymerization of thermoplastic additive

The mixture of clay and vinylene monomers (MMA and styrene) was prepared as follows. First, dried clay (6.3 phr based on the weight of vinylene monomers) was mixed with the raw reactants at 1000 rpm for 1h at room temperature, followed by high shear mixing at 7500 rpm for 15 minutes slow mixing at 500 rpm for 30 minutes, and then another 15 minutes at 7500 rpm. The copolymerization of MMA and styrene was initiated by adding 0.2 mol% of BPO, based on the mole of vinylene monomers, and carried out at 65°C under reflux in a nitrogen atmosphere while mixing at 300 rpm.

2.3 Hybrid polyester and nanocomposite preparation

The resin was mechanically mixed with the reaction products from in situ polymerization at 1000 rpm for 3h. MEKP (1wt % based on the weight of the UP/St/MMA system) was added

and the mixture was mixed for further 2 min under vacuum to remove air bubbles. The mixture was poured into molds, cured at room temperature for 12 h and post-cured at 110°C for 4h. In order to represent the relative amount of MMA and styrene present to act as curing agents we use the molar ratio (M/S). A ratio of 0.0 indicates that only styrene is present for curing. Simple nanocomposites were prepared by the direct mixing process. The clay was gradually added to the resin and mixed for 8h at 2000 rpm. The mixture was cast and cured following the same procedure as above.

2.4 Characterization Methods

Calorimetry was performed with a differential scanning calorimeter TA Q10 on 10mg of uncured sample in a hermetic aluminum pan. The isothermal reaction rate profile was measured at 25°C, followed by a scan from 25-300°C at a heating rate of 5°C/min to determine the total reaction heat.

X-ray diffraction analyses were performed using an X-ray diffractometer (Philips model X'PER) at the low angle range of 2θ with a scanning speed of 1 °/min. The X-ray source was Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$), using a 50 kV voltage generator and a 40 mA current. The nanostructure of nanocomposite samples were also examined with transmission electron microscopy (TEM) using a JEOL JEM-2100F microscope operating at a 200kV accelerating voltage. The samples were cut into thin sections (50-80 nm thickness) using an ultramicrotome with diamond knife.

Dumb-bell shaped specimens based on ASTM D638-82a (type V) were used to determine tensile properties on an Instron 3365 (5 kN) testing machine at a constant crosshead speed of 1mm/min. Fracture mechanic tests were carried out by MTS 312.21 (100 kN) according to ASTM D5045-99 on sharply notched three-point bend specimens at a constant crosshead speed of 10 mm/min.

The fracture surface of broken samples was coated by a thin layer of Pd for the microscopic characterization. A Hitachi S-4700 FE-SEM 2 kV scanning electron microscope was used to observe the fracture surface.

3 Results and discussion

3.1 In situ polymerization of thermoplastic component

During in situ free radical copolymerization of MMA and styrene, low conversion was desired where the total monomeric conversion was kept constant (around 20%) for all molar ratios of MMA to styrene. This corresponds to a thermoplastic content of 7wt% in the final cured hybrid system. It is known that at low conversions in this type of copolymerization [6] the molecular weight and molecular weight distribution are relatively insensitive to monomer molar ratios and that only the chemical composition of the copolymer is affected by the molar ratio of the monomers which is ignorable. Since polystyrene and PMMA are incompatible with UPR, their copolymer with different composition would be also incompatible.

3.2 Chemical reactions during solidification

During curing, unsaturated polyester resin and styrene undergo free radical copolymerization to form a three-dimensional network. The presence of a comonomer (MMA) makes curing more complex due to the number of different possible reactions including copolymerization of unsaturated polyester and styrene or MMA, copolymerization of MMA and styrene, as well as homopolymerization of each component. The probability of each reaction, during curing, can be estimated based on the monomer reactivity ratios of unsaturated polyester, styrene, and MMA [7]. Based on the reactivity ratios of the reactants, all copolymerization reactions dominate over homopolymerization with the exception of copolymerization between MMA and unsaturated polyester which is less likely than the homopolymerization of MMA. Also, the copolymerization between MMA and styrene is more likely than either styrene or MMA homopolymerization.

In order to evaluate the effect of MMA on the reactions during curing of simple polyesters, a series of isothermal DSC experiments were carried out at 25 °C. In the neat UPR reaction rate curve (Figure 1), we find two peaks; the shorter time peak is related to the crosslinking reaction between styrene and unsaturated polyester and the longer time peak is likely due to styrene homopolymerization. When MMA is present (the data is not shown), the long-time peak is eliminated indicating a significant reduction in styrene homopolymerization.

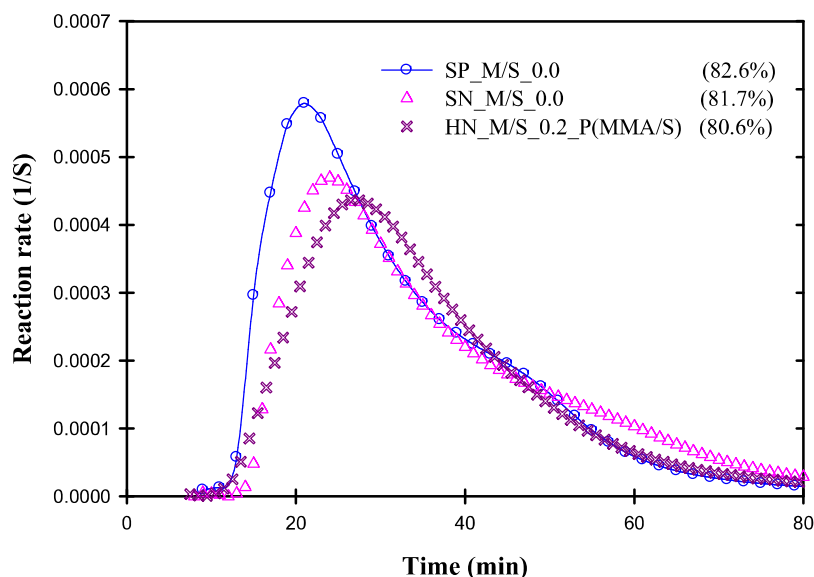


Figure 1. Effects of clay and P(MMA/S) on the curing reaction rate. For comparison the data for a simple polyester sample (SP_M/S_0.0), containing 0.2% BPO, is presented. All nanocomposite samples contain 2 phr clay. The hybrid system (HN_M/S_0.2_P(MMA/S)) contains 7 wt% thermoplastic. The final conversion of each system is given in parentheses in the legend

Next, the effect of MMA on the isothermal curing reactions of simple nanocomposites (2 phr clay) and hybrid nanocomposites was studied. In general, the presence of clay resulted in a reduction of the total reaction rate (Figure 1). The curing behavior of a hybrid system, containing a thermoplastic polymer, is complex due to phase separation of the system into thermoset-rich and thermoplastic-rich phases. In comparison to the simple nanocomposite (SN_M/S_0.0), the curing process is slower in the hybrid nanocomposite systems. Styrene

monomers easily diffuse into the thermoplastic-rich phase compared to the larger molecules of unsaturated polyester which are less compatible with the thermoplastic. Therefore, within this phase there is a high concentration of styrene but a low concentration of the polyester. As a result, the reaction rate in the thermoplastic-rich phase would be lower than in the unsaturated polyester-rich phase. In the presence of MMA, since MMA can diffuse quickly into the thermoplastic-rich phase, there is a high concentration of both styrene and MMA in this phase. As MMA/St copolymerization is faster than styrene homopolymerization, the total reaction rate inside the thermoplastic-rich phase increased resulting in a rise in the reaction rate in the whole system. However, there is an optimum MMA content because excess MMA can result in a decrease in unsaturated polyester conversion by consuming too much of the styrene.

3.3 Dispersion and distribution of the silicate layers

X-ray diffraction data for simple and hybrid nanocomposites illustrated that none of the nanocomposites exhibit the d_{001} diffraction peak at 25.5\AA characteristic of the original Cloisite 20A clay, indicating good delamination and dispersion of the silicate layers. The results also revealed that the in situ polymerization method led to an improvement in the degree of silicate layers delamination.

The state of dispersion of clay within the hybrid nanocomposite (HN_M/S_0.2_P(MMA/S)) was observed via TEM (Figure 2). The micrograph in Figure 2a indicates that the clay silicate layers are segregated within the thermoplastic-rich phase (particulate shape) in which they are partially arranged along the interface between the thermoplastic and thermoset phases. The micrographs show an intercalation/exfoliation structure. Inside the thermoplastic-rich phase, some small spherical particles can be observed which are surrounded by silicate layers. It appears these are unsaturated polyester-rich particles (microgel). Since well-dispersed silicate layers have tendency to locate in the interface of thermoplastic and thermoset phases, they surrounded unsaturated polyester-rich particles.

3.4 Properties

Tensile properties and the fracture toughness parameter (K_{Ic}) of our samples are summarized in Table 1. In the hybrid system, the presence of the dispersed organic phase decreased the tensile strength as compared to simple polyester due to poor adhesion at the interface of the unsaturated polyester-rich and thermoplastic-rich phases. Using the Takayanagi model Huang *et al.*[8] demonstrated that the tensile strength of UPR systems containing the thermoplastic phase is predominately determined by that of the major continuous cross-linked polyester phase. This means that, in the hybrid system studied here, tensile strength is mostly affected by crosslinking density. The molar ratio of M/S affects crosslinking density by changing the concentration of reactants (UP, MMA, and styrene) in thermoplastic and thermoset-rich phases. In other words, high concentration of MMA promotes MMA/St copolymerization resulting in a reduction in UP conversion. Therefore, this reduction decreases crosslinking density causing a reduction in tensile strength.

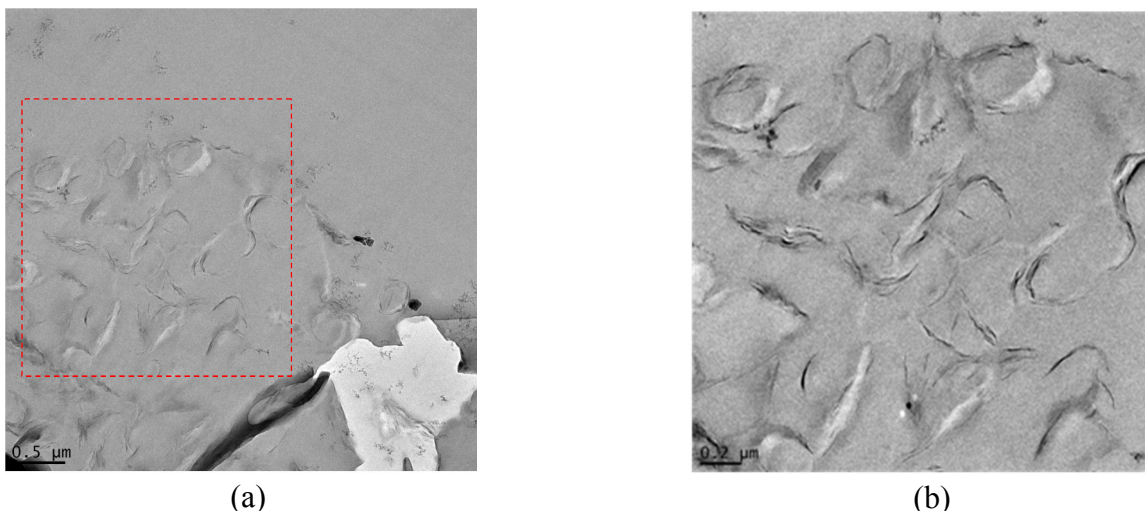


Figure 2. TEM images from the hybrid nanocomposite, HN_M/S_0.2_P(MMA/S). This sample contains 7wt% thermoplastic and 2 phr clay. The dashed box in (a) indicates the region enlarged in (b)

Sample	20A (phr)	Tensile strength (MPa)	Tensile modulus (MPa)	K_I (MPa.m ^{1/2})
SP_M/S_0.0	0	61.7 (2.7) ^b	986 (20)	1.23 (0.01)
SN_M/S_0.0	2	59.5 (1.3)	1030 (18)	1.36 (0.08)
HN_M/S_0.2_P(MMA/S)	2	51.0 (0.9)	948 (16)	1.87 (0.07)

^a The thermoplastic mass in the system is 7wt% in all cases.

^b The values in parentheses are standard deviations from 7 samples.

Table 1. Tensile properties and the fracture toughness parameter (K_I)

In the simple nanocomposite, clay slightly increased the modulus due to its high stiffness. The hybrid system approximately had the same modulus as the neat unsaturated polyester sample in spite of the presence of clay. In this system, the presence of MMA probably reduced the compactness of the network by increasing the length of crosslinking bridges. As a result, the modulus of the hybrid system is less than that of the simple nanocomposite.

The fracture toughness values, K_I , will turn out to be the most interesting property of our hybrid system. The addition of clay caused a slight improvement in toughness of the simple system as a result of the tortuous path for crack propagation (Figure 3a). However, this improvement is not as significant as that caused by both the thermoplastic additive and clay, HN_M/S_0.2_P(MMA/S), which the thermoplastic forms a second phase in the shape of spherical particles dispersed in the continuous unsaturated polyester-rich phase.

In the hybrid nanocomposite, silicate layers are predominantly located in thermoplastic-rich phase (Figure 2) resulting in an increase in the rigidity of the dispersed particles. Consequently, during fracture the particles behaved like rigid fillers and they remained intact after the fracture

(Figure 3b). As incorporation of particulate fillers into a thermosetting matrix can stabilize fracture by crack pinning mechanism, [9] the controlling mechanism of fracture toughness in the hybrid system is probably the same. However, debonding of the particles from the matrix is also likely which leads to a reduction of the effectiveness of pinning, but it can result in crack tip blunting and unstable propagation which leads to an increase in the fracture toughness [9].

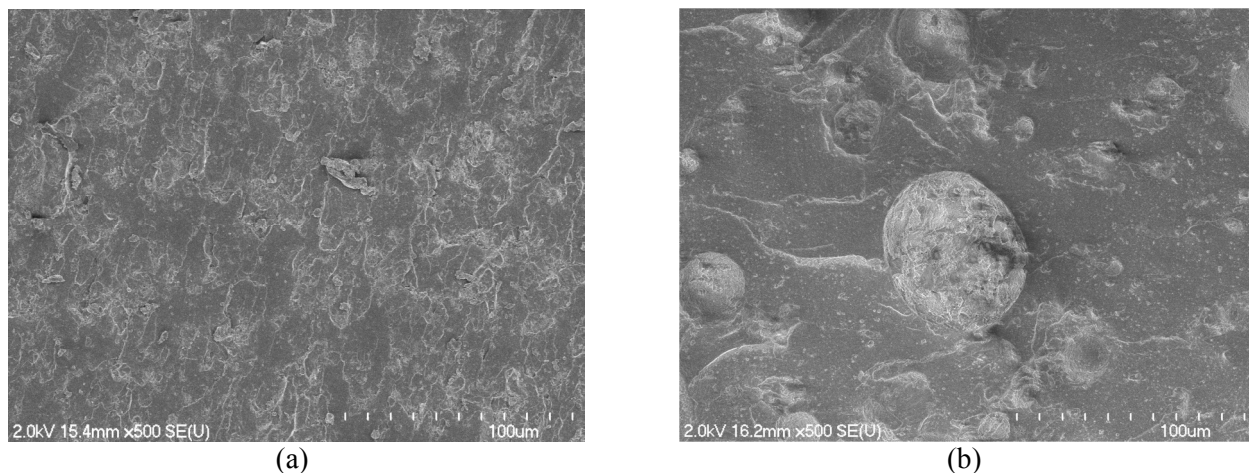


Figure 3. SEM micrographs of fracture surface of the simple nanocomposite (SN_M/S_0.0) and the hybrid nanocomposite (HN_M/S_0.2_P(MMA/S))

Therefore, the mechanism controlling fracture in the hybrid nanocomposite is complex with both blunting and pinning occurring simultaneously.

4 Conclusion

A new class of unsaturated polyester-based thermoplastic/thermoset hybrids and their layered silicate nanocomposites were developed. The approach provided an improvement in the degree of dispersion and delamination of the silicate layers. The silicate layers located in the thermoplastic-rich particles resulting in an increase in their rigidity. Consequently, a combination of thermoplastic and clay led to a synergistic improvement in fracture toughness of the thermoset matrix where the mechanism controlling fracture is complex with both blunting and pinning occurring simultaneously.

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