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Feasibility of Plasma Treated Clay in Clay/Polymer Nanocomposites Powders for use Laser Sintering (LS)

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Abstract. The addition of small quantities of nano-clay to nylon is known to improve mechanical properties of the resulting nano-composite. However, achieving a uniform dispersion and distribution of the clay within the base polymer can prove difficult. A demonstration of the fabrication and characterization of plasma-treated organoclay/Nylon12 nanocomposite was carried out with the aim of achieving better dispersion of clay platelets on the Nylon12 particle surface. Air-plasma etching was used to enhance the compatibility between clays and polymers to ensure a uniform clay dispersion in composite powders. Downward heat sintering (DHS) in a hot press is used to process neat and composite powders into tensile and XRD specimens. Morphological studies using Low Voltage Scanning Electron Microscopy (LV-SEM) were undertaken to characterize the fracture surfaces and clay dispersion in powders and final composite specimens. Thermogravimetric analysis (TGA) testing performed that the etched clay (EC) is more stable than the nonetched clay (NEC), even at higher temperatures. The influence of the clay ratio and the clay plasma treatment process on the mechanical properties of the nano-composites was studied by tensile testing. The composite fabricated from (3% EC/N12) powder showed ~19 % improvement in elastic modulus while the composite made from (3% NEC/N12) powder was improved by only 14%). Most notably however is that the variation between tests is strongly reduced when etch clay is used in the composite. We attribute this to a more uniform distribution and better dispersion of the plasma treated clay within polymer powders and ultimately the composite.

1. Introduction

The demand for materials that can solve weight and cost problems of metals in automobile and aerospace industry have raised interest in polymer-matrix nanocomposites. Unlike metals, polymers have desirable properties such as being easy to manufacture, light weight, and low cost, but their mechanical properties are limited compared to metals. To enhance the tensile strength and modulus of the polymers, reinforcements are incorporated in polymers in a low concentration ratio [1]. Nanoclay is one of the most interesting materials used as a reinforcement to enhance the strength and modulus of polymers [2]. However, the differences in degree of polarity and incompatibility between polymers and clays are limitations that restrict the strength of reinforcement. Hence, surface modification is used to render nanoclay miscible with polymer [3]. Since the early nineties, many studies have been conducted in polymer nanocomposites based on organically treated nanoclays.

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There have been few studies on the treatment of clay using the plasma processes [4, 5] and even fewer attempts have been made to prepare polymers nanocomposites based on plasma treated nanoclay [6, 7]. Polymer nanocomposites can be produced in either conventional (melt compounding) or non-conventional manufacturing (e.g. laser sintering) processes [8]. The weak interaction between clays and matrices and the agglomeration of clay particles are the main challenges for all methods. To a certain extent, organo-treated nanoclays have increased the mechanical properties of polymers in the conventional manufacturing methods such as melt compounding [9]. However, when laser sintering was used, the incorporation of Cloisite 30B (organically modified nanoclay) in Nylon12 in the laser sintering technique has reduced the strength and the elongation at break [11], see table 1.

Hence, the conventional modification of nanoclay for use in the laser sintering is not enough to render it compatible with polymers. Thus, this study aimed to investigate the effect of the air plasma treatment technique on the surface compatibility of the nanoclays with polymers. Downward heat sintering is used in this study to mirror the laser sintering process.

Table 1. Summary of results from previous studies on nylon 12 and nylon12/nanoclay composites (brackets relative change with regards to neat N12)

	Phang et al (2005) [9]	Yan et al (2011) [10]	Jain et al (2010) [11] ^b	Current study EC-based composite
Clay %	Elastic Modulus, MPa			
0%	1045±51.6	1420±250	736	853±28
1%	1110±25.8(6.2±5.5)%	xxx	xxx	xxx
2%	1140±77.4(9.1±8.9)%	xxx	xxx	xxx
3%	xxx ^a	1870±240(31.7±25)%	808.7(9.9%)	1011.7±10(18.6±3.5)%
5%	1480±100(41.6±10.9)%	xxx	755.7(2.7%)	998±17(17±3.9)%
Clay %	Tensile strength, MPa			
0%	33.56±0.18	38.3±2	49.15	39.58±0.68
1%	34.94±0.18(4.1±0.75)%	xxx	xxx	xxx
2%	34.75±0.18(3.5±0.75)%	xxx	xxx	xxx
3%	xxx	47.2±1.9(23.2±7.3)%	48.42(-1.5%)	42.95±0.41(8.5±2)%
5%	34.63±0.25(3.2±0.91)%	xxx	36.5(-25.7%)	40.3±0.35(1.8±1.9)%
Clay %	Elongation at break, %			
0%	xxx	20.8±2.8	27.82	24.17±1.27
1%	xxx	xxx	xxx	xxx
2%	xxx	xxx	xxx	xxx
3%	xxx	17.7±3(-15±19.8)%	14.62(-47.4%)	18.44±2(-23.7±9.9)%
5%	xxx	xxx	10.37(-62.7%)	9.17±1.3(-62.1±8.3)%

^a xxx means no data is available

^b Only absolute values are available in [11]

2. Materials

Polyamide 12 or Nylon 12 (trade name: Duraform PA2200; supplier: e-Manufacturing Solutions (EOS)) was used in this study as a matrix. Nylon 12 powder received had been used at least twice before in the laser sintering machines in the laboratories of the University of Sheffield. The chemical formula of Nylon12 is $(C_{12}H_{23}NO)_n$. The nanoclay used is organomodified montmorillonite (trade name: Cloisite 30B (supplier: Southern Clay Products) described further in [12].

3. Preparation Methods

3.1 Plasma treatment technique

Air/Oxygen Plasma treatment (also known as Plasma Etching) was used to treat C30B for ~30 minutes before adding the nanoclay to nylon 12. Plasma Cleaner Zepto from Diener Electronic is available in the Sorby Centre at the University of Sheffield. The nanoclay powder placed in glass petri dishes inside the chamber of the plasma cleaner was subjected twice to 100 % power and 2-4 mbar for 1000 sec. In the current study, the plasma treated clay is called as etched clay (EC) and the other clay is called as nonetched clay (NEC).

3.2 Dry Mixing

In atmospheric environment, 0.15, 0.25, and 0.35 gram of EC and NEC powders were added to 5 g of Nylon 12 powder in small glass jars. After that, the mixed powder was stirred in a magnetic stirrer for a half hour. Then the composite was sonicated in an ultrasonicator bath (model FB15051 made by Fisher company) for also half. Composition are summarized in table 2.

Table 2. The concentration of nanoclay (EC and NEC) in the nylon12 nanocomposite.

EC or NEC	nanoclay, g	N12, g	Comp.
NEC	0.15	5	3%NEC/N12
NEC	0.25	5	5%NEC/N12
EC	0.15	5	3%EC/N12
EC	0.25	5	5%EC/N12

3.3 Downward Heat Sintering

Downward heat sintering (DHS) in a hot press is used to process neat and composite powders into tensile and XRD specimens in order to reflect laser sintering conditions. Powders were placed in-between the two parts of the hot press. First, the powders is left in a hollow mould on the lower part (LP) for 15 minutes where the temperature of LP is just below the melting temperature (LP temperature is 185 °C for the neat N12 and 188 °C for N12 composites). Thus, the powder is preheated before the upper part (UP) goes down to generate a close heat chamber for another 15 minutes (UP temperature is 190 °C for the neat N12 and 193 °C for N12 composites). The temperature of the powder, is then raised to reach value above the melting temperature of N12. After that the powder being fully melted and the mould and samples are left to be cooled outside the hot press in at room temperature.

4. Characterization and Testing Techniques

4.1 X-Ray Diffraction (XRD)

XRD of powder was carried out using a Siemens D5000 (Cu, GAXRD) at room temperature from $2\theta = 2^\circ$ to 27° in a step of 0.02° and 1 sec per step. The machine was operated at 40 KV and 40 mA.

4.2 Thermogravimetric Analysis (TGA)

A Thermogravimetric Analyser (Pyris 1 TGA from PerkinElmer) was used. All powders were heated, in Nitrogen atmosphere, from 30 °C to 630 °C with a heating rate of 10 °C/min.

4.3 Scanning Electron Microscopy (SEM)

A Nova NanoSEM (Low Voltage Scanning Electron Microscopy (LV-SEM)) was used.

4.4 Tensile Testing

Tensile test was carried out using a Hounsfield Tensometer according to BS ISO 527. A 10000 N load cell, speed of test was 5 mm/min and a preload of 5 N were used.

5. Results and Discussion

5.1 XRD results

XRD patterns are shown in figure 1 (a). NEC exhibited a well-defined diffraction peak at 2θ of 4.8° and the interlayer spacing is equal to 1.8 (001 crystal lattice). While, the X-Ray scattered from EC gave a multiple peak at the same position of NEC, and the multiple peak tends to scatter more diffuse and have a low intensity peak than one sharp peak. Both NEC and EC spectra exhibited a weak peak with the same intensity at 2θ of 19.7° , and this is similar to what is reported in reference [7].

5.2 TGA results

Figure 1 (b) shows weight loss as a function of temperature. Organo-modified nanoclay is degraded in fourth stages, i.e. desorption of water, dehydration of hydrated cation, loss of surfactant, and dihydroxylation [13]. According to the results in figure 1 (b), all those steps were shifted to higher temperature compared with NEC. Hence, the EC is more stable than the NEC, even at higher temperatures.

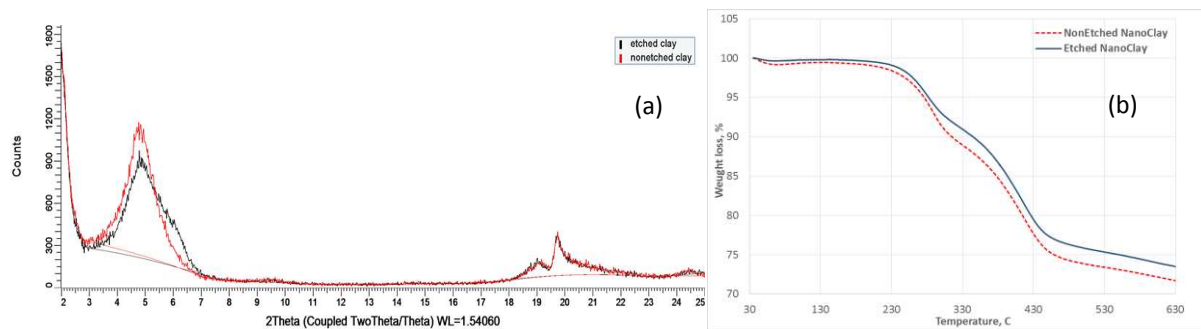


Figure 1. A comparison between the Etched and nonetched results using (a) XRD (b) TGA techniques

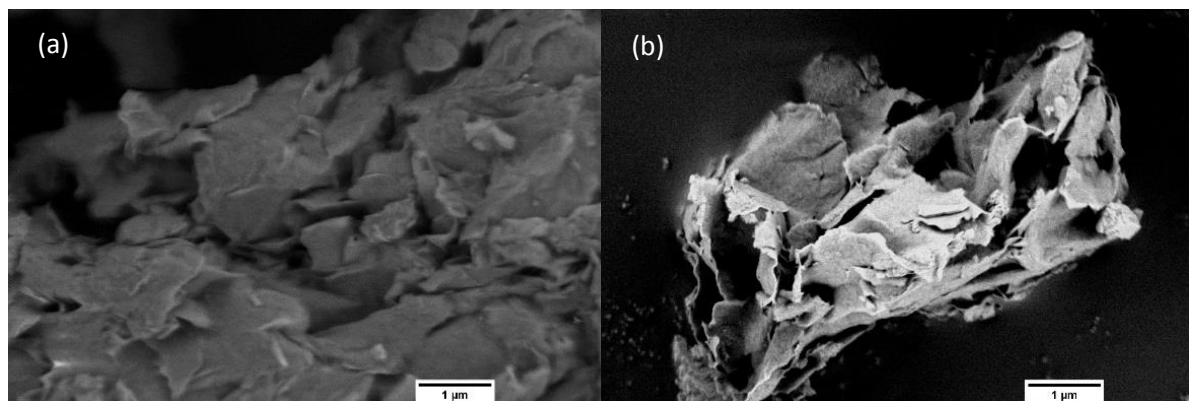


Figure 2. SEM images of (a) nonetched clay, and (b) etched clay

5.3 SEM images

The SEM images of NEC and 30 minutes treated EC are shown in figure 2 (a and b) respectively. Figure 2 (a) shows the clay platelets are stuck together which may result in non-uniform clay distribution. Non-uniform clay agglomerates on the surface of polymer particles and can weaken the strength of the composites [11]. Plasma treatment minimizes the sticking of clay platelets as shown in figure 2 (b).

5.4 Tensile test results

The tensile test results are presented in figures 3 and 4 (a). Adding the nanoclay (etched and nonetched) at concentrations 3% and 5% has improved the elastic modulus and tensile strength of N12 but leads to

a reduction in the elongation at break. It is important to consider the combination of these properties [14]. The best combination of all three properties is found for the 3% EC/N12 nano-composite. While the elongation at break was reduced by $\sim 24\%$ compared to neat nylon 12, the elastic modulus is increased by $\sim 19\%$ with a simultaneous increase in tensile strength of $\sim 9\%$. Both exceed the performance of clay/N12 laser sintered nanocomposites with the same clay loading reported in [11], see table 1. The reduction in the elongation is less pronounced for the EC/N12 nanocomposite ($\sim 24\%$) compared to $\sim 52\%$ for the NEC/N12 nanocomposite. For EC/N12, the fracture surface shows sign of ductility (see figure 4 (b)). The main reason for the reduced elongation and the brittle fracture is the adding of rigid clay [10]. In addition, the interaction between the clay and polymer is not strong enough to resist the axial force. This leads to the generation of microvoids [9] which develop to initiate a micro crack and the propagated cracks will lead to a brittle fracture. Based on this mechanism our results imply that the interaction between clay and polymer in the EC/N12 nanocomposite is stronger than that in NEC/N12 nano-composites. Also notable is that the variation between tests is strongly reduced when etched clay is used in the composite (see figure 3). We attribute this to a more uniform distribution and better dispersion of the plasma treated clay within polymer powders and ultimately the composite.

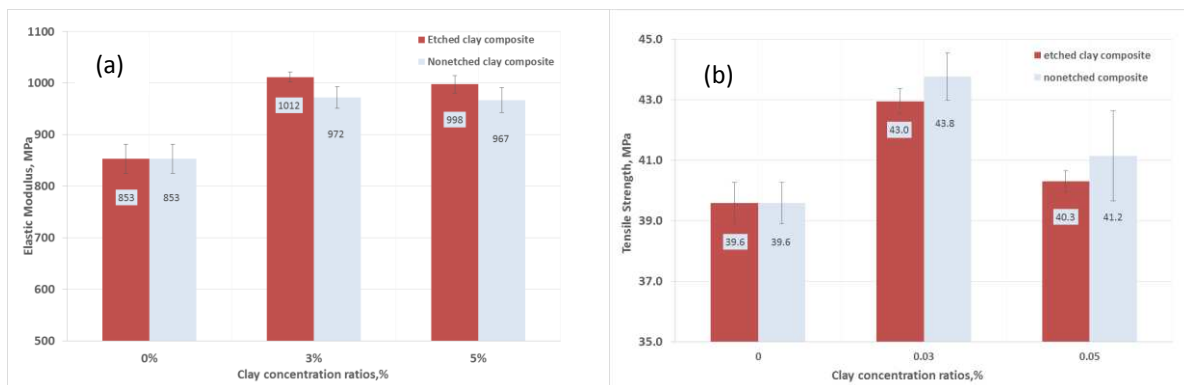


Figure 3. (a) Elastic modulus and (b) Tensile strength of EC and NEC based N12 composites.

At high filler loadings some of the clay platelets may not well disperse and that may negatively impact the tensile strength [11] and the elongation at break [9]. This seems to be the case for the 5% clay loading in our experiments, in which the elastic modulus is similar to materials with 3% clay but the tensile strength is hardly improved while the elongation at break was dramatically reduced by 62% (EC/N12) of the value of neat N12.

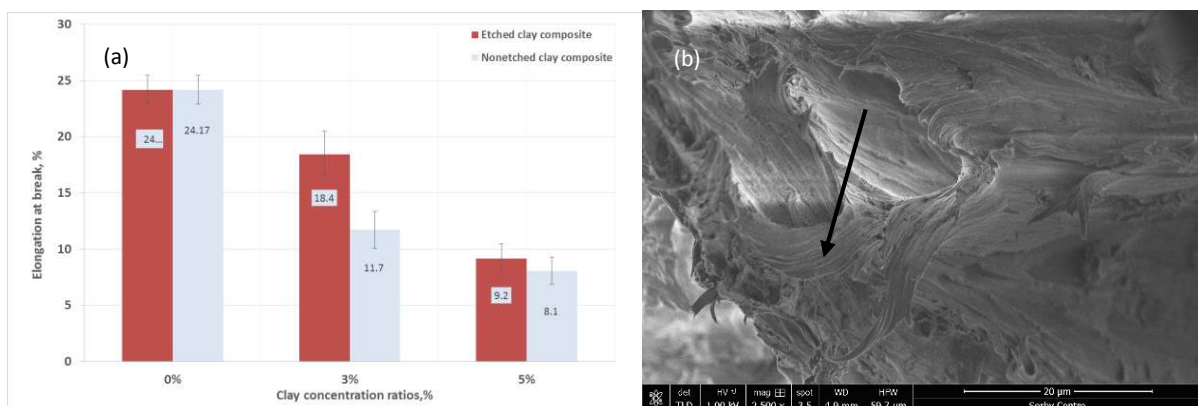


Figure 4. (a) The elongation at break values of N12 after adding etched and nonetched clay, (b) SEM image of 3%EC based nylon12 nanocomposite showing features of ductile fracture.

6. Conclusions

An improvement in the tensile properties (elastic modulus and tensile strength) when plasma treated organoclay is incorporated into non-virigin (powder used previously in laser sintering) nylon12 powder by a simple, dry mixing process is achieved. With this method, the tensile results after adding organoclay at concentrations of 3% or 5% are almost the same. However, in term of the cost of the material and the elongation of parts, the 3% based composite is the best. It means the method for making nanocomposite with enhanced properties at lower filler concentration is achieved.

The obtained polymer nanocomposites compare favourably to other mixing process and are encouraging for the use of dry mixed powders in Laser Sintering.

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