Nano-clay Reinforced Aramid Matrix Nano-composites – Fabrication and Characterization

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Abstract- The goal of the present work is to synthesize an aramid matrix followed by the fabrication of a novel class of nano-composites using a nano-clay as reinforcement. Aramid was first synthesized and functionalized by the solution polycondensation of aromatic diamines and diacid chloride in an amide solvent. Later, nano-clay was modified using amine organifiers to render the silicate layers organophilic. Six different loading fractions of the modified nano-clay were incorporated in the composites, i.e. 1wt%, 3wt%, 5wt%, 10wt%, 30wt% and 50wt%. The unique film forming abilities of aramid matrix-nanoclay composites at such high and low clay proportions were maintained. General trends depicted a decrease in moisture absorption and an increased thermal stability with an increase in clay content. The morphological properties, showing the dispersion of modified nano-clay in aramid matrix, were witnessed using FESEM. Moreover, TGA and DSC methods were used to evaluate the thermal properties of nano-composites. Finally, a separate experiment was conducted for evaluating moisture absorption of the nano-composite with different clay contents. This research work is driven towards the potential application of the fabricated nano-composite in the packaging industry.

Index Terms- Nano-Composite, Nano-Clay, Aramid, Morphological, Thermal, Dispersion, Intercalation, Exfoliation

I. INTRODUCTION

This project aims to explore the morphological, barrier, and thermal properties of a novel class of polymer-clay nano-composite. Nano-composites are polymers containing nano-fillers - nano-clay in this case. Nano-composites often demonstrate astoundingly unusual and beneficial properties making them multi-functional materials. Literature reports the usage of different nano-clay fillers with the purpose of performance enhancement in comparison to the pristine polymer matrix [1-8]. In the present study the microstructure of the nano-composites having nano silicate-layers was homogeneously dispersed in the aramid matrix. This caused an increase in interlayer spacing between nano-silicate layers ultimately improving the thermal, barrier and morphological properties.

II. PROCEDURE

A. Standards and Materials

The objective of this research is to synthesize a novel aramid matrix followed by the modification of the nano-clay to render it organophilic and fabrication of the polymer-clay nano-composite.

The monomers used for the matrix synthesis include two different diamines - and a diacid chloride. A diamine was used for clay modification. All the chemicals were procured from Aldrich and used without further purification. The Montmorillonite (MMT) clay reinforcement was selected for nano-composite fabrication. All the materials were kept and used under completely anhydrous conditions.

B. Synthesis of Aramid Matrix

An aromatic polyamide was synthesized by the solution polymerization of aromatic diamines and diacid chloride under anhydrous conditions. Two diamines were dissolved in an amide solvent under inert atmosphere. Solution was stirred for 6 hours for complete mixing. After complete mixing was achieved, stoichiometric amount of the diacid chloride was added to the diamine solutionat 0°C to avoid any side reaction due to highly exothermic reaction. Additional 24 hours were given for reaction completion. Finally the reaction mixture was viscous and brown in color. The aramid was acid functionalized by adding 1% excess of diacid chloride with further stirring for 6 hours. The structure of the synthesized aramid was characterized by FTIR spectroscopy. The following scheme shows the reaction equation involved in the synthesis of the aramid (Ar) matrix. Considering the molar ratios:

$$x\ \text{diamine-1} + y\ \text{diamine-2} + n\ \text{acid chloride} \rightarrow z\ \text{Aramid}$$

where

$$n = x + y \text{ and } z = x + y + n$$

C. Clay Modification

Nano-silicates were organically modified by a cation exchange reaction between Na-MMT and the diamine. Na-MMT was dispersed in water at 80°C. The organo-modifier was dissolved in water at 80°C and a stoichiometric amount of concentrated HCl was added to the solution. Dissolved silicates were added to the solution of the modifier and this mixture was agitated vigorously for 3 h at 60°C. The blackish gray precipitates were isolated by suction-filtration and washed with 400 ml hot water. The filtrate was treated with 0.1M $AgNO_3$ until there were no AgCl precipitates, thus ensuring complete removal of the chloride ions. The final product obtained by filtration was dried in a vacuum oven at 60°C for 24 h. The dried cake of amine modified MMT was ground and screened.

D. Fabrication of Nano-Composites

Nano-composites were fabricated by taking a measured amount of aramid matrix solution in a flask, followed by the addition of a known proportion of modified organo-clay. The reaction mixture was agitated at high speed for 24 h in order to achieve uniform dispersion of nano silicate platelets in the polyamide matrix. The amount of amine modified MMT was varied from 1 to 50wt% in the nano-composites. Thin and uniform composite films were cast in Petri dishes by pouring the polymer-clay hybrid solution, followed by solvent evaporation at high temperature under vacuum.

III. RESULTS

E. Spectral Analysis

FTIR was performed to confirm incorporation of modified nano-silicate layers. FTIR spectra of both pristine aramid and its nano - omposite were compared. The presence of Si-O bond was confirmed by the presence of broad bands in the range of 700-1100 cm^{-1}, [6] which were absent in pristine matrix. Presence of a broad band at 3383 cm^{-1} validated the hydrogen bonded amide N-H bond. Thus, FTIR analysis of pristine polymer and the nano-composite film confirmed the incorporation of silicate layers into the aramid matrix.

F. Thermal Properties

The glass-transition temperature (T_g) was taken as the midpoint of the change in the heat capacity in DSC studies. Melting temperature (T_m) was taken as the maximum of the endothermic peak. The successive increase in clay content depicted an increase in glass transition temperature. Additionally, TGA results augmented the DSC analysis and demonstrated an increased value of the degradation temperature with the increasing clay content.

G. Morphological Analysis

FESEM analysis was performed for different samples of nano-composite containing different clay content. The objective of this study was to assess the morphological changes in the nano-composite samples thus evaluating the nature of interaction and dispersion of silicate layers in the aramid matrix. Fig. 1 shows the FESEM micrographs of the modified nano-clay composites.

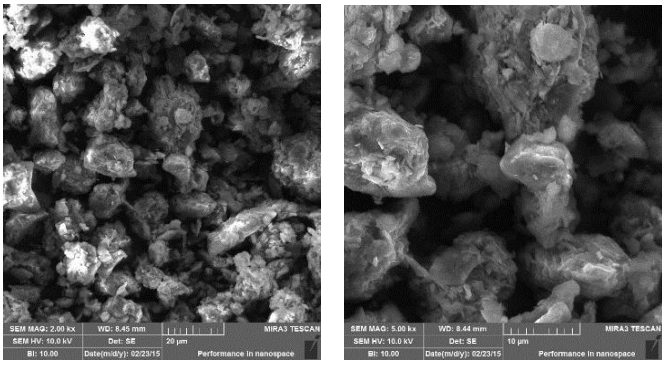

Figure 1 FESEM Micrographs of Nano-Clay composites

H. Water Absorption

The water absorption test for the nano-composite was carried out using ASTM technique D5720, to evaluate and compare the water uptake of pristine aramid and aramid/amine modified MMT nano-composites. The samples were taken in dried form and their initial weight (W_d) was measured using digital weight balance. Then the samples were soaked in water for a period of 24 hours. During this period the mass of the samples increased. The samples were removed from water and their final weight (W_f) was evaluated using digital weight balance. The percent increase in weight of the samples was then calculated using the following formula: $(Wf - Wd)/Wd$

As the amide matrix contains amide linkages in the backbone that have the tendency to uptake water through hydrogen bonding, thus, in the water absorption studies it was revealed that the incorporation of nano-silicate layers in the aramid matrix resulted in a decrease of water absorption as compared to pristine aramid as depicted in Fig 2. Water permeability or water absorption depends on nature, incorporation and dispersion of nano silicate layers. Results show that an increase in clay concentration resulted in an enhanced barrier property to moisture absorption of nano-composites. This decreased water permeability can be attributed to the exfoliated nano-clay layers that effectively caused an increase in the diffusion pathways i.e. mean free path available for diffusion [4].

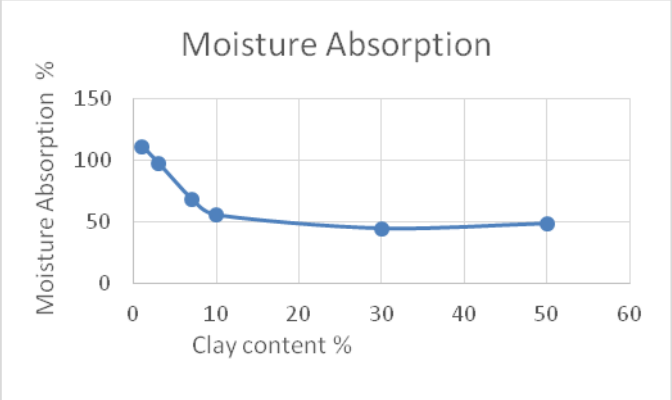

Figure 2 Moisture Absorption relative to Clay Content in Nano-Composite

IV. DISCUSSION

Optimum thermal and morphological profiles were depicted by the nano-composite containing 30-wt. % clay content. TGA and DSC results demonstrated an increased thermal stability with increasing clay content. The dispersion of nano-clay layers enhanced certain barrier properties including moisture absorption. The incorporation of nano-silicate layers in the aramid matrix was observed using FESEM micrographs which confirmed a good dispersion of the nano-clay in the aramid matrix.

V. CONCLUSION

A novel class of aramid/amine modified MMT nano-composites was successfully fabricated via solution intercalation route. The uniform dispersion of the modified organo-clay throughout the aramid matrix was confirmed using FESEM micrographs. Enhanced morphological, thermal and barrier properties of aramid/clay nano-composites were observed which increased significantly with increasing clay content into. Barrier property and thermal stability drastically enhanced with organo-clay because the modified nano silicate layers act as the mass diffusion barrier to water molecules and volatile degraded products.

VI. REFRENCES

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