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Abstract

This paper addresses the effects of operating variables on mechanical properties of polyester/clay nanocomposites including tensile strength, percentage elongation etc. The variables were clay type, clay content, and prepolymer–clay mixing type. The experiments were carried out based on the design of experiments using statistical methods. The nanocomposites were synthesized via in situ polymerization of polyester and clay (dissolved using styrene monomer) with Methyl-ethyl ketone peroxide (MEKP) as catalyst in Cobalt base accelerator. Unmodified Kaolinite clay and Vinyl silane modified clay are the two types of clay examined. The parameters studied, clay type and mixing method are found to have significant effects on mechanical properties. Polyester nanocomposites showed larger improvements in mechanical properties compared to pristine polyester, especially when sonicator type of mixing is employed due to the favorable shear forces exerted by polymer matrix on clay aggregates during polymer–clay mixing. It is observed that the stress and elongation at break of the nanocomposite samples can be optimized with a particular percentage of clay loading. Characterizations of the nano composites were also made using techniques like SEM.

***Keywords**: Polyester, Nanocomposites, Clay, Exfoliation, Mechanical properties*

INTRODUCTION

In recent years polymer nanocomposites have attracted extensive interests around the world due to the many superior properties they offer compared to traditional micro-size composites [1–3]. One of the most promising polymer nanocomposite systems is a hybrid based on organic polymers and inorganic clay minerals consisting of layered silicates. Crystal lattice of montmorillonite (MMT), widely used in nanocomposites, consists of two-dimensional layers in which a central octahedral sheet of alumina or magnesia is fused to two external silica tetrahedrons. Many studies involving MMT clay has been done so far. This paper is based on study conducted using Kaolinite clay, which is much more difficult to intercalate or exfoliate do to it's low swelling and shrinkage capacity.

Obviously the studies done so far using kaolinite clay are less. Due to its difficulty in dispersion, we try to introduce a higher degree of dispersive technique using Sonicator, where in which we try to achieve intercalation to exfoliation (or near exfoliation) of clay dispersion. Kaolinite is a clay mineral, part of the group of industrial minerals, with the chemical composition $Al_2Si_2O_5(OH)_4$. It is a layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedra. Also the effect of vinyl silane, a coupling agent modified clay on the polyester resin is examined. Thus the clay is supposed to be made more hydrophobic.

Polyesters have widespread applications as fibers, clothing's, ropes Bottles etc. These polymers possess good mechanical properties such as high abrasion resistance, tear strength, flexibility and elasticity and outstanding oil resistance [12, 13]; however, it is possible that these properties could even more be improved by using organophilic nanofillers. The various processing methods used to prepare polyester nanocomposites cause different filler distribution and exfoliation of the clay layers. The structure of polyester matrix as well as the type of hydrophobic cation in the clay can alter the variety of properties in Polyester/clay systems [5].

Thus the clay dispersion in the Polyester matrix, and therefore the ultimate properties of nanocomposite could be influenced by the factors including the process variables such as the type or molecular weight of polyol in Polyester structure, the type of cation (modifier) and the content of clay,[3,9,10] and mixing parameters.[10–12] The experimental design using the Design of Experiments (DOE) method is a statistical approach for investigating the effects of various parameters on the product quality and/or quantity. This method also screens the significant factors affecting the response from those with less significance, and gives the optimum condition to attain the most desirable performance [13]. There are less reports available regarding the application of experimental design for comparative analysis of the effects of operating variables on the mechanical properties of Polyester/clay nanocomposites. In this study, the influences of prepolymer type (A), clay content (B), mixing type (C) and clay cation (D), on the mechanical properties of Polyester/clay nanocomposites have been investigated.

EXPERIMENTAL

Unsaturated polyester resin, MEKP and Cobalt accelerator is obtained from Sharon Nest Engineering, Kochi and is used in the ratio of 100:1:1 percent weight. The clay unmodified and modified (90mequiv/100g clay) were obtained from Alpha chemicals, Kochi. The lab grade styrene monomer used to dissolve clay has been imported from USA through chemical point, Kochi. The supplementary data as received from the supplier is also available.

Design of experiments

The first important step in the design of experiment is the proper selection of factors and their levels. In this study, the operating factors like mixing method, clay content, and clay type were considered. The factors and their levels have been chosen according to the literature review on previous publications, the practical aspects, and some screening experiments.

Preparation of Polyester/clay Nanocomposites

For the preparation of nanocomposites, 100g of polyester resin was first degassed and then poured into a flask equipped with a mechanical stirrer/sonicator and a constant temperature water bath. Specified amount of dried clay (unmodified/vinyl modified dissolved in styrene monomer) powder was dispersed in the resin under vigorous stirring. The mixing time in this step was set to the designed value of 15min. The specified amount of MEKP and Cobalt base accelerator was then added as a chain extender to the prepolymer/clay mixture under vigorous stirring for the specified time.

The system was degassed and immediately poured into a Teflon coated mold where the curing was performed for 24hrs at room temperature. Post curing for a standard time of 10hrs at a standard temperature of 80C is also employed. The Polyester/clay nanocomposite specimen was finally removed from the mold. A same procedure was applied in the preparation of pristine polyurethane without adding any clay. Also sets of specimen utilizing ordinary stirring have also been molded.

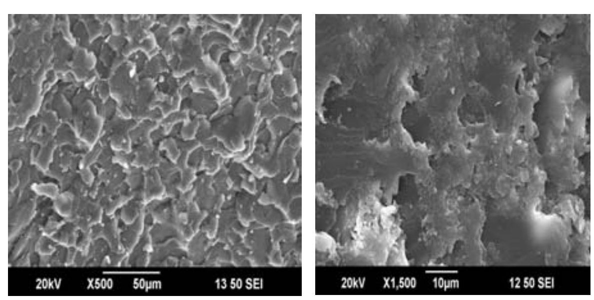
Characterization and property measurements

The tensile test has been performed on high precision machines according to ASTM standards. SEM characterization technique has been employed to understand the clay dispersion.

RESULTS AND DISCUSSION

Characterization

Characterization done using SEM shows significant improvements in clay dispersion to achieve exfoliated or near exfoliated structure when higher degrees of mixing methods has been employed. Analyzing the micrographs given below, it is clear that an exfoliated structure has been achieved by using sonicator dispersive technique (Figure 1.1 c) when compared to intercalative dispersion using mechanical stirrer technique (Figure 1.1 b). Figure 1.1a shows the SEM for a manually dispersed nanoclay/polyester structure where an absence of a proper dispersive technique is evident.



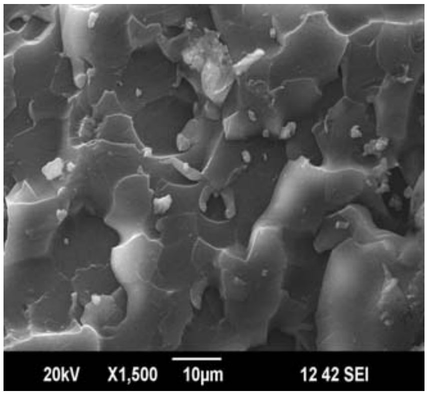


Figure 1.1 Scanning electron micrograph for specimen prepared using (a) Manual dispersion, (b) Mechanical dispersion and (c) Sonicator dispersion

Influence of operating variables

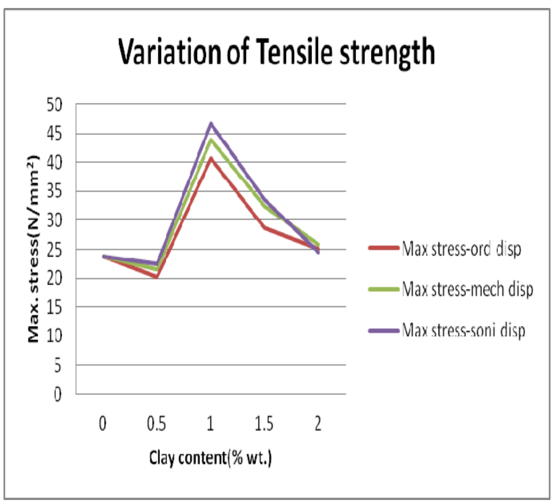


Figure 1.2 Graph showing variation in Tensile strength for various percentage of unmodified clay content

The trends in which the mechanical properties are influenced when the factors are varied on their levels are shown on main effects (Table 1.1 and Table 1.2) as well as interaction plots. (Figure 1.2 - Figure 1.5).

Clay type

It is implied that the original pristine sample results in weak improvements in tensile properties compared to that of organoclays. Properties of Vinyl modified samples shows slight improvement especially in the vicinity of optimal clay loading range, when compared to unmodified nanoclay composites.

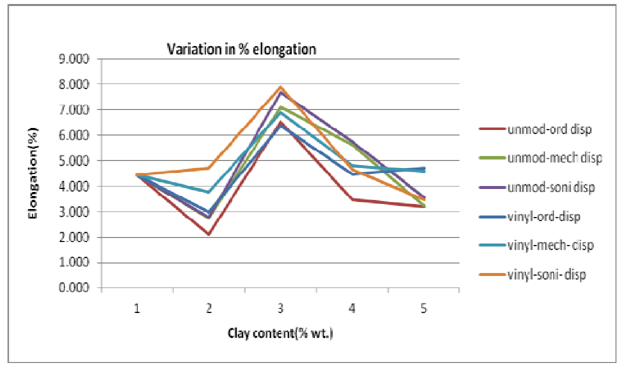


Figure 1.3 Graph showing percentage elongation for both Vinyl modified and unmodified clay contents

Clay content

It is observed that the stress at break and percent elongation represent the highest improvement with a particular percent of clay loading (1%). The silicate layers of clay play their reinforcing action in the polymer matrix, and this is increased with clay content up to the percent the clay cannot be exfoliated anymore.

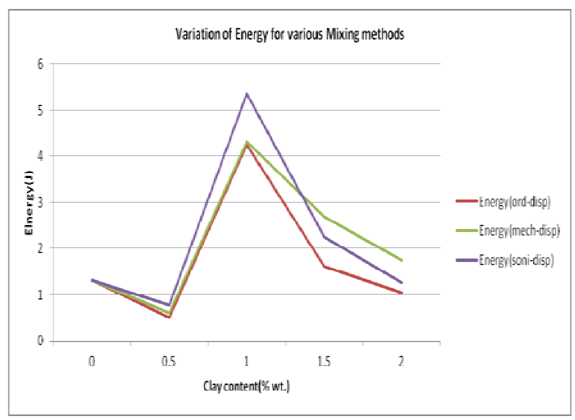


Figure 1.4 Graph showing variation in strain energy for various percentage of unmodified clay content

Mixing Method

The mixing method and its intensity are vital in the preparation of exfoliated morphology in polymer clay nanocomposites; it seems that the intensity of mixing with a high shear impeller used in this work has accelerated enough the kinetics of intercalation of polyester chains into the galleries and even the exfoliation of silicate layers throughout the polymer matrix.

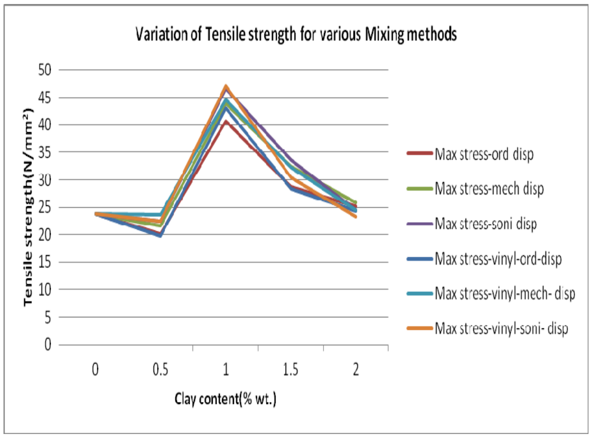


Figure 1.5 Graph showing variation in Tensile strength for various percentage of unmodified and Vinyl modified clay content

Table 1.1 Table showing Tensile strength data and Strain energy for various percentage of unmodified clay contents prepared using various mixing methods

TYPE	Max.Stress(N/mm2)-S		Energy(J)-J		Average	
	Replication1	Replication2	Replication1	Replication2	S	J
0.5%UNMOD-MAN	20.1873	20.0872	0.50298	0.50656	20.13725	0.50477
0.5%UNMOD-MECH	20.0872	23.0614	0.50656	0.71535	21.5743	0.610955
0.5%UNMOD-SONI	23.3949	21.4855	0.8947	0.64827	22.4402	0.771485
1.0%UNMOD-MAN	40.8947	40.5546	3.61093	4.90455	40.72465	4.25774
1.0%UNMOD-MECH	43.2762	44.4498	2.91037	5.72563	43.863	4.318
1.0%UNMOD-SONI	45.4892	47.7453	4.9939	5.71113	46.61725	5.352515
1.5%UNMOD-MAN	26.0894	31.2698	1.11456	2.11953	28.6796	1.617045
1.5%UNMOD-MECH	31.2698	33.6232	2.11953	3.24862	32.4465	2.684075
1.5%UNMOD-SONI	32.489	34.748	1.52155	2.97593	33.6185	2.24874
2.0%UNMOD-MAN	25.2868	24.9545	0.93074	1.16965	25.12065	1.050195
2.0%UNMOD-MECH	28.6619	23.0024	2.50869	0.98294	25.83215	1.745815
2.0%UNMOD-SONI	25.1461	23.9883	1.29555	1.22979	24.5672	1.26267
PURE	23.4486	24.1207	1.31277	1.31052	23.78465	1.311645

Table 1.2 Table showing Tensile strength data and Strain energy for various percentage of Vinyl modified clay contents prepared using various mixing methods

TYPE	Max.Stress(N/mm2)-S		Energy(J)-J		Average	
	Replication1	Replication2	Replication1	Replication2	S	J
0.5%vylMOD-MAN	19.9506	19.4886	0.83269	0.55994	19.7196	0.696315
0.5%vylMOD-MECH	24.6641	22.7362	2.06575	1.00336	23.70015	1.534555
0.5%vylMOD-SONI	21.3226	23.7149	1.34116	1.44354	22.51875	1.39235
1.0%vylMOD-MAN	43.3838	42.6884	3.67105	3.78956	43.0361	3.730305
1.0%vylMOD-MECH	44.757	44.4498	4.27257	5.72563	44.6034	4.9991
1.0%vylMOD-SONI	47.4892	46.5812	5.4312	5.482	47.0352	5.4566
1.5%vylMOD-MAN	28.1718	28.6796	1.60609	1.617045	28.4257	1.6115675
1.5%vylMOD-MECH	31.7382	32.9318	1.89561	2.01736	32.335	1.956485
1.5%vylMOD-SONI	28.147	32.7683	1.8	2.013	30.45765	1.9065
2.0%vylMOD-MAN	24.9137	23.6817	1.43729	0.94979	24.2977	1.19354
2.0%vylMOD-MECH	24.0875	24.8132	0.91884	1.1256	24.45035	1.02222
2.0%vylMOD-SONI	22.3094	24.2508	0.88696	0.96659	23.2801	0.926775
PURE	23.4486	24.1207	1.31277	1.31052	23.78465	1.311645

CONCLUSIONS

The influences of various operating variables on the mechanical properties of Polyester/clay nanocomposites were statistically analyzed. The main conclusions that are valid in the range of levels considered in this study are as follows:

- The mechanical properties strongly depend on the prepolymer type, the clay cation, the clay content and mixing method investigated in this study.
- Polyester nanocomposites show more improvements in mechanical properties compared to pristine ones due to higher shear forces exerted by polymer matrix on clay aggregates during polymer–clay mixing.

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