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PRODUCTION OF PHENOLIC RESIN / LAYERED SILICATE NANOCOMPOSITES

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ABSTRACT

Polymer/layered silicate nanocomposites having phenolic matrix were produced. The method of production was melt-intercalation. This method consists of mixing the modified montmorillonite clay with phenol formaldehyde resin mechanically, and curing the polymer to form a nanocomposite material, via intercalation of polymer in between the clay galleries and the exfoliation of these layers homogenously throughout the matrix. The effect of several parameters such as different resin structure, cure treatments, clay type, clay modifier and amount are examined by a full characterization of the produced specimens using x-ray diffraction, mechanical tests and electron microscopy. Further trials are still being carried out to examine the effects of any change in processing parameters.

Keywords: Phenolic resin, Layered silicate, Nanocomposite

1. INTRODUCTİON

Polymer layered- silicate nanocomposites are new hybrid polymeric materials with the layered silicates in the form of sheets of one to several nanometers thick and hundreds of nanometers long. Due to the unique nanometer-size dispersion of the layered silicate with high aspect ratio, high surface area and high strength in the polymer matrix, nanocomposites generally exhibit improvements in properties of polymeric materials even at very low volume fraction loading (1-5%) of layered silicates in contrast to the high volume fraction loading (~50%) in the traditional advanced composites. [1]

Although the intercalation chemistry of polymers when mixed with appropriately modified layered silicate and synthetic layered silicates have long been known [2,3], the field of polymer layered silicate nanocomposites has gained momentum recently. Two major findings have stimulated the revival of interest in these materials: first the studies of the Toyota research group on Nylon-6 / montmorillonite nanocomposites [4], for which very small amounts of layered silicate loadings resulted in pronounced improvements of thermal and mechanical properties; and second, the observation of Vaia *et al.*[5] that it is possible to melt-mix polymers with layered silicates, without the use of organic solvents. Today efforts are being conducted globally, using almost all types of polymer matrices [6].

Phenolic resins, both resols and novalacs, haven't been paid enough attention as possible nanocomposite matrices, especially when compared to the huge number of studies carried out on other thermoset polymers such as epoxy resins. This is partially due to the difficulty of the task; phenolic resins have a 3-D structure even prior to cure, which makes exfoliation of the clay with the polymers difficult. Also, the heat treatments of the liquid phenolic resins are quite long and sensitive; when compared to problemless epoxy. Because of these reasons, there are very few studies on phenolic resin / layered silicate nanocomposites [7,8,9,10,11,12], but none of these studies involve production of this type of materials from liquid phenolic resin. In this present study, the main objective was to optimise the process of producing resol type phenolic resin/layered silicate nanocomposites from liquid resins.

There are several parameters which have an effect on the final chemical and physical condition of the composite material to be produced. The effect of resin type, clay type, clay percentage and curing method on the amount of exfoliation of the clay layers and mechanical and thermal properties of the nanocomposites are investigated and an optimum processing flow sheet has been prepared. For characterization of the nanocomposite materials produced, x-ray diffraction analysis and mechanical tests were carried out.

2.EXPERİMENTAL

2.1 Materials

The phenolic resins used, Polifen76 and Polifen76TD, were kindly provided by Polisan Co (Turkey). Both of these resins, Polifen 76 (PF76) and Polifen76TD (PF76TD) are water based resol type phenolic resins, the latter also containing some monoethylene glycol(meg) and diethylene glycol(deg) for the effect of plasticizing. Some physical properties of these resins are given out in Table 1.

Three different types of clays were used to prepare the nanocomposites. Rheospan®AS (Nanomer I.33M), which is alkyl dimethyl benzyl ammonium modified montmorillonite clay, was purchased from Nanocor Inc.; Cloisite ® Na+, which is unmodified sodium montmorillonite, and Cloisite ® 10A, which is benzyl tallow dimetyl ammonium modified montmorillonite were both purchased from Southern Clay Products. Properties of these clays were published elsewhere [13,14,15]

P-toluenosulfonic acid was used in acid curing of the resin; and it was purchased from Merck.

2.2 Sample Preparation

One of the main goals in this study was to figure out the best processing route for the resol / layered silicate nanocomposites, which would provide optimum properties for the nanocomposite specimens. By the end of the research, two different procedures were found, one for heat curing of the resin and the other for the acid cure of the resin.

Specimens which were cured only by the appliciation of heat, were prepared by a long heat treatment lasting for about 3 days. The clay and the resin were first mechanically mixed for 2.5 hours at 50°C and then ultrasonically mixed at 50°C for 1h. Following that, the mixture was poured into molds and put into the furnace at 60°C for 24 hours. Then, the temperature of the furnace was raised to 80°C and the specimens were kept at that temperature for another 24h. After, the temperature was further raised to 100°C for 10 hours and the treatment was completed by a post-cure treatment at 130°C for 1h.

Specimens which were cured using p-toluen sulfonic acid, were prepared in a much shorter period of time. The resin and clay were first mechanically mixed at 55°C for about 30 min and then

ultrasonically mixed at 55°C for another 30 min. After that, the stoichiometric amount of acid is added and the mixture was further mixed mechanically for another 2h. Following that, it was poured into the molds and placed in the furnace at 70°C, and stayed there for 3h. Following a post-cure treatment at 130°C for 1h, the specimens were ready.
Following these procedures 8 specimens were produced. The compositions of these specimens are given out in Table 2.

2.3 Characterization

X-ray diffraction(XRD) is one of the most effective tools in determining the level of intercalation or exfoliation, in polymer / layered silicate composites. In this study, XRD Analysis of the specimens were carried out using a Rigaku diffractometer, with CuKα radiation, at a general voltage of 30kV and a general current of 15mA. Scanning was in continous steps at a speed of 5 deg/min, scanning a 2θ range of 0 to 10deg in specimens 1 through 8. The clays were also put in XRD analysis and the results are also tabulated.

Mechanical tests were carried out to determine flexural strength and charpy impact toughness of the specimens. All the tests were carried out according to ISO standards.

3. RESULTS AND DİSCUSSİON

As a result of XRD analysis, flexural tests and charpy impact tests the following results are obtained:

3.1 XRD Analysis

XRD diffractogram can be examined in Figures 1-4. Figure 1 shows the x-ray diffractogram of neat phenolic resin; which gives a very broad peak, characteristic of amorphous materials. In Figure 2, which is the analysis of Rheospan clay, it is seen that the d-spacing of the clay is ~27.6A at 2θ =3.2°.
Figure 3 shows the XRD pattern of specimen D3, in which it is seen that the peak of the clay at 2θ =3.2° have been vanished, meaning that exfoliation has occured.

3.2 Mechanical Properties

Following the production of the specimens, two different mechanical tests were carried out; 3-point bending test and charpy impact test. The results are given in Table 3.

3.2.1 Amount of Clay Loading

When the clay percentage is increased, the mechanical properties tend to increase up a limit concentration, which was found to be 0.5% of rheospan in this case. It is seen from Figure 4 that, both flexural strength and impact strength increase up to 0.5% of clay loading by 10.2%; and then the amount of increase drops from 10.2 % to 4.8% as clay amount is incresead to 1%. Above 1% the clay layers start to form tactoids, decreasing the mechanical properties by considerable amounts.

3.2.2 Type of Resin Used

Of the two resins available, PF76TD has several advantages over PF76. The cure cycle is much shorter and the amount of bubbles formed during curing is much lower. It is seen from the mechanical tests that the mechanical properties of PF76TD is also higher than that of PF76 (Figure 5).

3.2.3 Method of Curing

One advantage of resol type phenolic resins over novalac type phenolic resins and also on other thermosetting polymers is the ability of the resin to be cured solely by the application of heat as well as by the presence of an acid. This fact arises the question: which type of cure treatment will give the better mechanical properties? It can be seen from Figure 6 that acid cure gave out the better results when the clay type, resin type and all the other parameters were kept constant. This was most probably due to the agglomaration of clay particles during the long heat cure cycle, which is approximately 60 hours. In contrast, no agglomaration was observed in acid cured samples; which took approximately 7 hours.

3.2.4 Effect of Modifier

It is very well known that modified clays give better results with most of the polymers, resulting in intercalation of the polymer molecules into the gallery spacings and finally the exfoliation of the layers. But it is also published in several papers that this may come out to be false in some cases; especially when the modifying chemicals have dislike moleculer structures than the polymer itself. That is why, in the present study Rheospan, which is actually montmorillonite modified with alkyl dimethyl benzyl ammonium salt, was compared with unmodified Na-montmorillonite. It was seen that modification helps intercalation and exfoliation considerably. The increase in flexural and impact strength can be examined below in Figure 7.

4.CONCLUSİON

In the view of all these results, it was seen that resole type phenolic resin / organically modified clay nanocomposites could be produced from liquid resins and exfoliation was achieved.

The best results were obtained using PF76TD resin which is basically resole type phenolic resin having monoethylene glycol and diethylene glycol.

Also, the best mechanical performance was seen at very low clay loadings, such as 0.5 to 1%. Over 1% clay layers started forming aggloromates, which caused mechanical properties to drop.

Although heat cure is also possible, acid cured samples gave out far better results, and when the amount of time required for heat curing is also considered, acid cure stands up alone as the best cure method to prepare nanocomposites.

Nanocomposites with alkylammonium modified clays gave out better results than unmodified clays; which was probably due to the larger gallery space in between the clay layers of modified clays.

Further trials are still being carried out to create a model for the exfoliation mechanism of the nanocomposites.

5. REFERENCES

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TABLES

Table 1
Physical Properties of the Resins Used

	Viscosity(cPs, 20°C)	pH(20°C)	Density(g/cm_3)	Free phenol/formaldehyde (%)
PF76	800 – 1100	7.5 - 8.5	1.215 - 1.230	3% / 5%
PF76TD	800 – 1100	7.5 - 8.5	1.210 – 1.225	2% / 3%

Table 2.
Specimens Produced

Specimen#	Resin	Cure method	Clay	Clay %
D1	PF76	ACID	-	-
D2	PF76TD	ACID	-	-
D3	PF76TD	ACID	RHEOSPAN	1%
D4	PF76TD	HEAT	CLOISITE 10A	1%
D5	PF76TD	ACID	CLOISITE 10A	1%
D6	PF76TD	ACID	CLOISITE Na+	1%
D7	PF76TD	ACID	RHEOSPAN	1.5%
D8	PF76TD	ACID	RHEOSPAN	0.5%

Table 3
Mechanical Performance of the Specimens

Specimen	Flexural Strenght (MPa)	Impact Strength (kJ/m^2)
D1	97,3	0.725
D2	99,8	0.883
D3	104,6	1.019
D4	50,5	0.689
D5	68,0	0.664
D6	98,1	0.740
D7	90,9	0.844
D8	110,0	1.059

There are several conclusions to be drawn, examining these results:

FIGURES

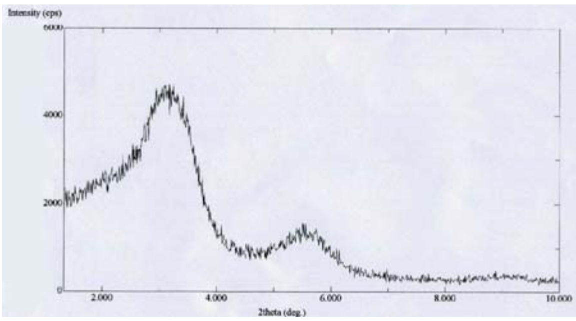

Figure 1. XRD pattern for the neat resole

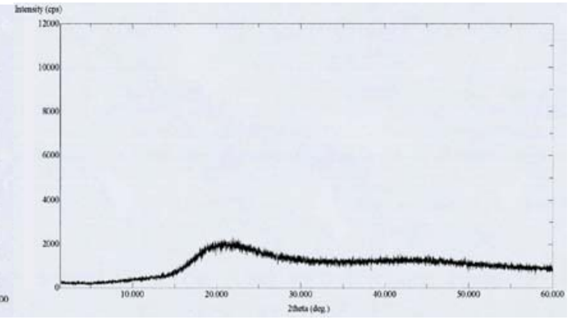

Figure 2. XRD pattern for rheospan clay

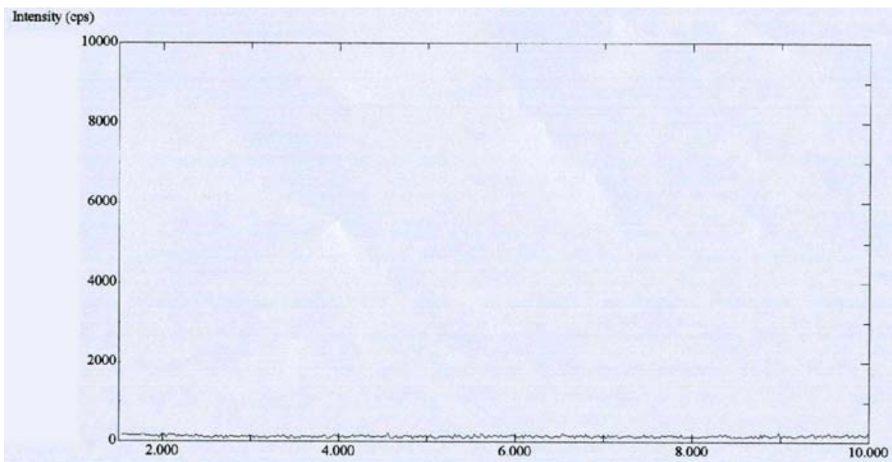

Figure 3. XRD pattern of specimen D8.

	D2 neat resin	→	D8 0.5%R	→	D3 1%R	→	D7 1.5%R
Flx. Strg.	99.8 MPa	+10.2%	110.0 MPa	+4.8%	104.6 MPa	-8.9%	90.9 MPa
Imp. Strg.	0.883 kJ/m^2	+19.9%	1.059 kJ/m^2	+15.4%	1.019 kJ/m^2	-4.4%	0.844 kJ/m^2

Figure 4. The effect of clay percentage on flexural and impact strength of specimens

	D1 PF76 (a.c.)	↔	D2 PF76TD (a.c.)
Flx. Strg.	97.3 MPa		99.8 MPa
Imp. Strg.	0.725 kJ/m^2		0.883 kJ/m^2

Figure 5. Mechanical properties of the two resins used

	D4 (acid cure)	D5 (heat cure)
Flx. Strg.	50.5 MPa	68.0 MPa
Imp. Strg.	0.689 kJ/m^2	0.664 kJ/m^2

Figure 6. Effect of cure treatment on mechanical properties

	D6 1%Na+ (a.c.)	D3 1%Rheospan (a.c.)
Flx. Strg.	50.5 MPa	104.6 MPa
Imp. Strg.	0.689 kJ/m^2	1.019 kJ/m^2

Figure 7. Effect of alkylammonium modification on mechanical properties