Investigation of Thermal Properties of PUF/colored Organoclay Nanocomposites

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Recently PF resins can be also prepared by the addition of urea because urea accelerates cure process of PF resin, reduces the cost and improves its strength performance. Clays have long been used as inorganic fillers in polymer systems because of low cost, availability and improved thermal properties of resulting polymer composites. Clay nanocomposites of different types yield a marked increase in a number of properties of thermoplastic and other resins and composites. This study investigates the variation of thermal properties of PUF/colored organoclay nanocomposites with increased colored clay ratio. For this the DSC, XRD, FT-IR and HRTEM analyses were made. The XRD patterns and HRTEM images showed that clay platelets were exfoliated at the lower contents of organoclay, whereas at the higher content of organo clay tactoids were observed. The XRD analysis results implied that the amorphous behaviour increased with increased content of colored organoclay. The DSC thermograms indicated that glassy transition temperature (T_g) was increased, appearing prominent crystallization peaks at the lower ratios of organoclay. The T_g value was partially decreased and the peak intensities gradually decreased with increased content of clay. The thermogram for composite with clay content of 20% was similar to the thermogram of virgin resin. This can be attributed to the shifting of the textural structure for this composite from prominent crystalline structure to amorphous one.

1. Introduction

Phenol-formaldehyde, urea-formaldehyde, and melamine-formaldehyde are the most important members of the thermosetting resins [1–4]. Phenol–formaldehyde (PF) resins, as the first true synthetic polymers made from the reaction of phenol with formaldehyde, have been widely used in various applications for more than 50 years [1]. Recently, urea has been introduced into PF resins to improve their curing, to lower the content of free formaldehyde, and to reduce the cost of the resin. This resulted in additional reactions, additional structures and more complicated compositions in PUF resins [5]. PUF synthesis is the two-step polymerization process, by which the trimethylolphenol (TMeP) is formed in the first step and in the second step urea is bonded to TMeP. Thus, both cross-linked PF and cross-linked PUF resins are located in the reaction stage.

Polymer/clay nanocomposites often provide significant mechanical, thermal, and physicochemical property improvements at small (0.5–5 wt.%) clay loadings versus the pristine matrix polymer or conventional clay-filled composites (micro and macrocomposites) [8]. It was investigated preparation and characterization of syndiotactic 1, 2-polybutadiene/organoclay nanocomposites [9]. The XRD shows that exfoliated nanocomposites are formed dominantly at lower clay concentrations (less than 2%), at higher clay contents intercalated nanocomposites dominate. At the same time, the XRD spectra also indicate the present of the crystal structures of nanocomposites. The researchers examined the effect of clay amount on mechanical properties of phenolic resin/layered silicate nanocomposites and suggested that the best mechanical performance was seen at very low clay loadings, such as 0.5 to 1% [10]. Over 1% clay layers started forming agglomerates, which caused to drop the mechanical properties. It was synthesized and characterized the layered silicate composites having phenolic matrix [2]. The XRD patterns showed that there was a decrease in amorphous behavior with increasing filler content. Tensile and flexural modulus increased up to 84 and 46%, respectively, of the initial value with increase in filler content up to 0.8%, after which there was a downward trend due to possible agglomeration of clay particles. We have tried to examine layered silicate composites having PUF matrix because of a limited number of studies related with this resin and also the lack of studies related to the use of colored organoclay as filler. This study aims to investigate both the variation of thermal properties of PUF/colored organoclay nanocomposites with increased colored organoclay ratio and the mechanisms of the interactions between the exfoliated or intercalated clay platelets and the polymer chains based on the FTIR spectra, the XRD patterns, the DSC thermograms and the HRTEM images.

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2. Experimental

2.1 Material

Solid urea, phenol, and aqueous solution of formalde-hyde (37%), NaOH, and HCl which were used in the synthesis of PUF composites, supplied from Merck. In order to prepare the colored organoclays, raw clay from Erzurum region in Turkey was used. The physical properties of the raw clay are given in Table I. The cation exchange capacity (CEC) of clay was determined by the methylene blue test (ANSI/ASTM C837-76). Chemical composition of the raw clay was determined by XRF spectrometry (see Table II). Cetyltrimethylammonium bromide (CTAB) as a cationic surfactant that was purchased from Merck was used without further purification. Remazol Red RB (C.I: Reactive Red 198) as a dye stuff, which is a commercial reactive textile dye [11].

Some physical properties for the raw clay in this study*.   TABLE I

CEC [meq/100g]	d [g/cm^3]	OMC [%]	w_L [%]	w_P [%]	I_p	a [m^2/g]
48.9	2.61	5.10	102.00	35.00	67.00	64.20

*(CEC) cation exchange capacity, (d) density, (w_L) liquid limit, (w_P) plastic limit, (I_p) plasticity index, (OMC) organic matter content, (a) specific surface area.

TABLE II
Chemical compositions of clay.

SiO$_2$	Al$_2$O$_3$	CaO	MgO	Fe$_2$O$_3$
45.12	13.70	7.48	7.29	5.63
K$_2$O	Na$_2$O	TiO$_2$	SO$_3$	P$_2$O$_5$
2.62	2.37	0.53	0.44	0.25

2.2 Preparation of colored organoclay Phenol-Urea-Formaldehyde (PUF) resins and colored organo clay-Phenol-Urea-Formaldehyde (COPUF) composites

In this study, in order to prepare of colored organoclay, 10 g of raw clay was added to 5 L of an aqueous solution of CTAB (240 mg/L) plus Remazol Red RB (50 mg/L). The mixture was then filtered, dried and sieved through a sieve of 200 meshes. PUF/colored organoclay composites were prepared by in situ intercalative polymerization of Phenol-Urea-Formaldehyde, (PUF) using phenol (18.2%), urea (36.3%) and formaldehyde (45.5%) in the various ratios of colored organoclay (3.22–20.0%). The preparation procedure was as follows: phenol was mixed with formaldehyde (as a 37% formalin solution) and urea in a glass reactor equipped with a mechanical stirrer, a thermometer and a reflux condenser and then synthesized colored organoclay in a given ratio was added to the mixture at 70°C. Finally, the resulted mixture was stirred for 1 hour and the viscous mixture following after adding a few drops of concentrated HCl was pelleted mechanically in 2.0 tons/cm^2. The PUF resin and the PUF/colored organoclay are coded as PUF and COPUF1-5, respectively. Their compositions are given in Table III.

The compositions of PUF composites including the colored organoclay   TABLE III

PUF composites	Phenol [wt.%]	Urea [wt.%]	Formaldehyde [wt.%]	Colored clay [wt.%]
PUF	18.2	36.3	45.5	—
COPUF1	18.2	36.3	45.5	3.22
COPUF2	18.2	36.3	45.5	6.25
COPUF3	18.2	36.3	45.5	9.10
COPUF4	18.2	36.3	45.5	14.30
COPUF5	18.2	36.3	45.5	20.00

2.3 Characterization of PUF resin and COPUF composites

Many techniques such as FTIR, XRD, HRTEM and DSC have been incorporated to characterize the resin and the nanocomposites in this study. XRD diffractograms for the resin and nanocomposites were taken in Rikagu SmartLab X-ray Diffractometer with a CuK$_\alpha$ (1.540 Å) radiation, operating at 40 kV and 30 mA over a 2θ range of 3–40°. The scanning rate of the instrument was 2°/min. FTIR spectra for prepared pure resin and nanocomposites were taken on a Perkin-Elmer Spectrum-One, by KBr pelleting method from 4000 to 400 cm^{-1}. The all measurements were obtained by an average of 100 scans and a resolution of 1 cm^{-1}. The specimens from the samples were examined by using aJEOL JEM 2100F High Resolution Transmission Electron Microscope operated at 200 kV. The curing behaviors of PUF resin and COPUF nanocomposites were observed with a differential scanning calorimeter (Exstar DSC7020) under nitrogen atmosphere. A typical sample weight was about 10 mg and the scan speed was 20 °C/min.

3. Results and discussion

3.1 FTIR analysis

FTIR spectra for PUF resin and the composites containing the various ratios of colored organoclay are given in Fig. 1. The peak at 3300–3400 cm^{-1} is associated
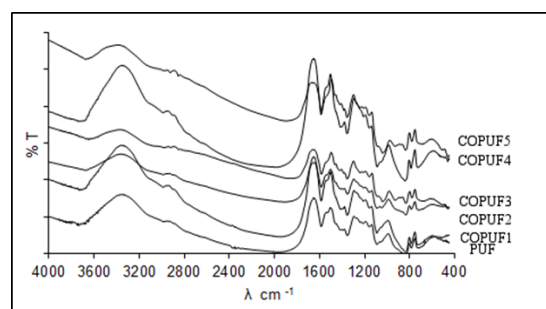

Fig. 1. FTIR spectra for PUF resin and the composites.

with stretching vibration of methylol-OH. The peak isn't

observed both FTIR spectrum of PUF resin and the composites. This indicates that the crosslinking is preventing vibration of -OH group for PUF resin and the composites. The peaks at 2970–2874 cm^{-1} are associated with in phase stretching vibration of -CH$_2$ hydrocarbon tails of CTA$^+$ ions, out of phase stretching vibration of -CH$_2$-hydrocarbon tails of CTA$^+$ ions, respectively. The spectra of composites coded COPUF3-5 exhibit two adjacent peaks at this range. This can be attributed to the tactoidal dispersion of clay platelets in which have intercalated the polymer chains. The peaks at 1417–1420 cm^{-1} can be attributed to aromatic -C=C- symmetric bending belongs to phenolic rings. The peaks at 1041–1091 cm^{-1} that are associated with -C-O-C- etheric bridges were observed at same intensity in all the composites. The peaks at 838–845 cm^{-1} that are associated with para substituted benzene were observed with similar intensity in all the composites, indicating multiple crosslinking in the polymer matrix. The peaks at 810–790 cm^{-1} corresponding to vibrations of the C-Cl belongs to the dye stuff doesn't exhibit any significant shift with the increase in the ratio of colored organoclay. Thus, it can be said that these groups not affected from the polymerization.

3.2 XRD and HRTEM analyses

The XRD and TEM are frequently used to characterize morphology of nanocomposites [12–15]. Figure 2 shows the XRD patterns for the PUF resin and COPUF (1–5) composites. The pattern for the PUF resin exerts a broad band containing two sharp peaks. These two sharp peaks adjacent the broad peak of the amorphous structure can be attributed to the present of two different crystalline structures in the polymeric framework. It may be suggested that the first crystalline peak corresponds to the cross-linked chain blocks of PF, while the second crystalline peak belongs to the cross-linked chain blocks of PUF. In the case of COPUF1 and 2, the lack of the first peak may indicates that the crystal framework of the cross-linked chain blocks of PUF in these composites predominated after the exfoliation of the colored organoclay platelets homogenously dispersed in the resin matrix (Fig. 2a and b). At the higher ratios of colored organoclay it was observed that the characteristic peak of the clay appeared to be shifted to the left. This indicates the present of tactoidal dispersion, due to intercalation of polymer chains into the interlayer region of the clay (Fig. 2c, d, e and f). On the contrary, it was reported that pure resole resin composite sample showed a highly amorphous behavior and showed very small peaks in the XRD pattern. It was observed that there was a decrease in amorphous behavior with increase in the clay content [2]. The HRTEM micrographs for the composites coded COPUF (1–5) are shown in Fig. 3, where the dark lines represent the clay layers, and the gray clouds represent the resin matrix [15, 16].

From Fig. 3 it can be concluded that the exfoliated organoclay platelets heterogeneously dispersed in the polymeric matrix, whereas at high colored organoclay ratios, the tactoidal dispersion of colored organoclay particles in the polymer framework began to dominate. For the resole type phenolic resin/layered silicate nanocomposites, it was suggested that clay distribution is homogeneous up to clay content of 1.5% [17].
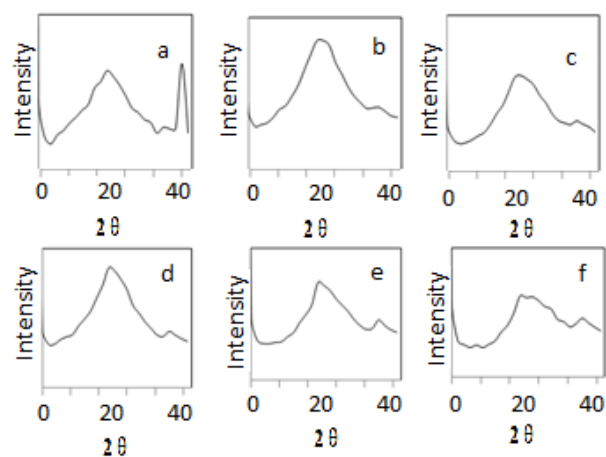

Fig. 2. The XRD patterns of PUF resin (a) and COPUF (1–5) composites (b, c, d, e and f).
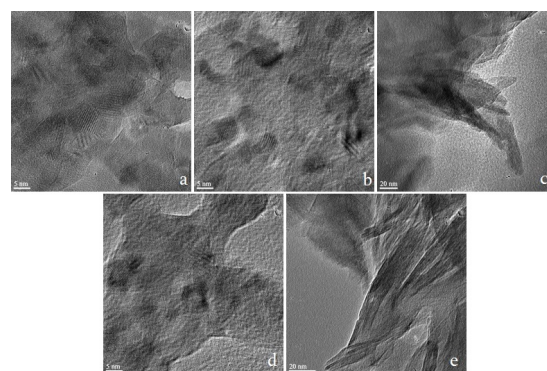
Fig. 3. The HRTEM micrographs for COPUF (1–5) composites (a, b, c, d and e).

3.3 DSC analysis

The characteristic temperature range of the DSC curves gives valuable information on the cure reaction of resins [1]. The DSC curves for the virgin PUF resin and PUF/colored organoclay composites are shown in Fig. 4. From this figure, it can be seen that the PUF resin exhibited clear glassy transition behavior, as well as a melting endotherm that appeared at a very high temperature. This can be attributed to both crystalline and amorphous nature of the PUF resin. The broad melting peak or the overlapped two peaks can be correlated with two crystal peaks adjacent to the broader amorphous peak that has appeared at XRD diffractogram of the resin.

From DSC curves of the composites synthesized at the lower ratios of colored organoclay (COPUF1-2), it was observed that these composites exhibit the higher glassy

transition temperatures comparing with the virgin resin (PUF), as well as sharp crystal peaks. This indicates that the clay platelets covered with the polar dye ions in connection with CTA$^+$ ions adsorbed onto the clay surface are completely exfoliated into the resin matrix, and oriented the polymer chains to a suitable conformation to crystal formation. It was reported that for phenolic resins, the dramatic increase of the T_g is due to the strong interfacial interaction between the silicate nanolayers and phenolic matrix, which reduces the molecular mobility of the matrix molecules [18]. The researchers investigated variation of glassy transition temperature during curing, and suggested that the changing of T_g value of a cross-linked system is related to the conversion of reacting groups [19]. Also, they have accepted that the change of T_g is dependent on the various parameters (the molar mass, the stiffness and the free volume entrapped in the network). In the literature, it was argued that the chemical bonding at the interface of the clay and epoxy matrix could hindered relaxation mobility in the polymer segments near the interface, which lead to the increase of T_g [20]. This figure, also shows that the intensive exother-
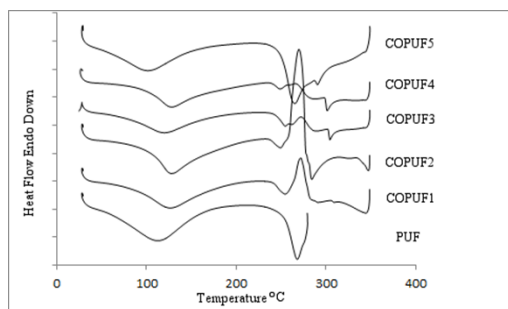

Fig. 4. The DSC thermograms of PUF resin and COPUF (1-5) composites.

mic peaks, corresponding to crystallization behavior of the synthesized composites with the higher ratios of the colored organoclay (COPUF3 and 4), appeared, as well as the T_g values decreased. This could be attributed to the heterogeneous distribution of the small stacks of clay plates or the separated clay platelets into the polymer matrix and to the dominant effect of the dispersion characteristics on the chain conformation, which could lead to crystallization. Again, it can be seen from this figure that the thermogram belonging to COPUF 5, which contains a broader melting peak or the overlapped two peaks at higher temperature has exhibited a thermogram similar to that of the virgin PUF resin. In addition, it can be said that the synthesized composite with the highest ratio of the colored organoclay exhibited an amorphous behavior depending on the higher clay content, and so the broader melting peak appeared.

4. Conclusions

Phenol urea formaldehyde resin (PUF)/colored organoclay nanocomposites have been synthesized by using in situ polymerization technique with a common textile dye, Remazol Red RB, PUF resin and organoclay prepared using CTAB. The main results obtained from this study are summarized as follows,

- The variation of thermal properties of PUF/colored organoclay nanocomposites with increased colored clay ratio has been investigated by considering the DSC, XRD, FT-IR and HRTEM analyses.

- The XRD patterns and HRTEM images showed that clay platelets were exfoliated at the lower contents of organoclay, whereas at the higher clay content of organo tactoids were observed. The XRD analysis results implied that there was an increase in the tending to amorphous behaviour with increased content of colored organoclay.

- The DSC thermograms indicated that glassy transition temperature (T_g) was increased, appearing prominent crystallization peaks at the lower ratios of organoclay. The T_g value was partially decreased and the peak intensities gradually decreased with increased content of clay. The thermogram for composite with clay content of 20% was similar to the thermogram of virgin resin. This can be attributed to the transition of the textural arrangement for this composite from predominant crystalline structure to amorphous one.

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