Microhardness and Surface Charge Correlation in Resol Phenolic Resin/Organoclay Composites

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Abstract – **For the preparation of resol phenolic resin/ organoclay composites (ROC), the resol phenolic resin (RPR) in which the synthesis conditions were 50°C and 1.3 F/P (Formaldehyde/Phenol) ratio was used. At the synthesis of organoclay (OC), a surfactant, cetyltrimethylammonium bromide (CTAB), was used as the modifier. For this, the Na Montmorillonite clay (MMT) with 2:1 layered structure was modified by using the aqueous solutions of CTAB at its different initial concentrations, and surface charge of the OC particles was controlled by zeta potential measurements. The in situ polymerization technique was used in the preparation of composites. The synthesized ROC composites were characterized morphologically and structurally by using technique as optical microscope (OM). Also, with microhardness analysis, the change of mechanical properties of the ROC composites and with the sign and density of the surface charge of the OC was investigated. The results demonstrated that the mechanical behavior of the ROC composites prepared was dependent on the sign and density of the surface charge of OC layers.**

Keywords – **Composite, Microhardness, Organoclay, Resol Phenolic Resin, Surface Charge.**

I. INTRODUCTION

Various filler materials are used for the purpose of decreasing the cost in the production of the composite materials attained with phenolic resins and ensuring wider usage of these materials by adding them properties such as hardness, strength, dimensional stability, saturation, resistance to heat, damping and sealing [1-3]. The properties of the composites to which filler materials have been added are determined with the properties of the components forming the composites, shape of the filler phase, morphology of the system and polymer-filler interfacial interactions [4-5]. Clays are from the widely used inorganic filler materials due to the fact that they have a layered structure, that could be easily found and they have low cost [6]. It is necessary for the clay layers to be welldispersed within the polymer matrix for giving the desired properties to the composite materials [7]. However; it is not possible for the layers to be efficiently and homogenously distributed within many polymer matrixes due to the tactoidal distribution tendencies of the clay layers. Also; the incompatibility of the hydrophilic silicates and hydrophobic polymers prevents the layered distribution of the tactoids. For this reason; the layered silicates are organically modified for the purpose of producing the clays in more accordance with the polymers. It is necessary for the surface-active substances such as alkylammonium

should take the places of the spaces in the silicate structure or the inorganic changeable cations in the galleries for the clay surface to be in accordance with the hydrophobic polymer matrix [8-9]. After the attainment of the organoclay, polymer/clay composite materials are produced with the methods of in-situ polymerization and solution and melt blending [8]. The polymer/organoclay composites produced with the use of clay continue to be the centre of attention due to their superior properties such as mechanical strength, resistance to heat and gas permeability when compared to the pure polymers especially as a result of the attainment of the exfoliate structure [9-10]. In this study; ROC composites have been prepared with in-situ polymerization technique with the use of the MMT modified in different initial CTAB concentrations (OC) and phenolic resin at 50ºC preliminary polymerization temperature and by the ratio of 1,3 F/P (RPR). The relation between the microhardness properties of the ROC composites and the surface charge of OC has been examined.

II. MATERIAL AND METHOD

Na-Montmorillonite (MMT) clay with 2:1 layered structure and supplied from the city of Cankiri in TURKEY has been used in the preparation of the OC. XRD diffractogram of the MMT is given in Fig. 1. The peak (distance (d) is 1,23 nm) observed at $2\theta = 7,19°$ in the diffractogram given in this Fig. 1 reflects the characteristic peak of MMT whose smectite group has 2:1 layered structure [2]. MMT has been modified in natural pH (7.8) and 150 rpm stable mixture speed, in different initial CTAB concentrations (80, 120, 160, 180, 200, 240, 260, 280, 300 mg/L), for 60 minutes, at 20°C stable temperature and by the ratio of 0,08g /100mL (solid/liquid) for the synthesis of the OC with different surface charge [11[DFM1]]. The codes and zeta potential values of the OC prepared in different initial CTAB concentrations are given in Table 1.
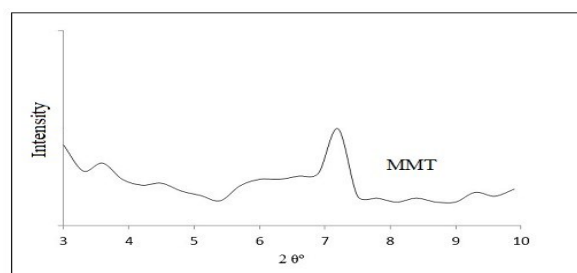

Fig. 1. XRD diffractogram of the MMT.

Table 1. Sample codes, the initial CTAB concentrations (C_0) and zeta potential values (ζ) of the OC.

Samples	C_o (mg/L)	ζ (mV)
MMT	-	-31,2
OC80	80	-30,8
OC120	120	-29,3
OC160	160	-27,2
OC180	180	-24,8
OC200	200	-17,6
OC240	240	-4,5
OC260	260	+7,0
OC280	280	+16,7
OC300	300	+21,0

2,0 g phenol and 6,44 mL formaldehyde (F/P=1,3) have been added to the three-dimensional glass balloon inside the water bath at 50ºC and the pH of the mixture has been adjusted to 9 with 40% of NaOH solution. OC prepared in different initial CTAB concentrations has been added in a way that the OC content in the mixture will be 1% in weight and the mixture has been magnetically mixed for 2 hours under the condenser. The liquid mixtures produced with in situ polymerization have been taken to the circular molds with the dimension of 2 cm and dried for 10 hours at 70ºC under vacuum. The synthesis conditions and codes of the RPR and the ROC composites are given in Table 2.

Table 2. Synthesis conditions and codes of the ROC composites.

Samples	F/P	T (ºC)	Organoclay
RPR	1,3	50	-
ROC501	1,3	50	OC80
ROC502	1,3	50	OC120
ROC503	1,3	50	OC160
ROC504	1,3	50	OC180
ROC505	1,3	50	OC200
ROC506	1,3	50	OC240
ROC507	1,3	50	OC260
ROC508	1,3	50	OC280
ROC509	1,3	50	OC300

XRD diffractograms of the OC and ROC composites have been taken with the use of Cu radiation based Rigaku branded Smart Lab model device. Diffractograms have been attained from the samples in dusty state at the scanning area of 2θ = 1,5-40º and at the scanning speed of 2º/minute. The zeta-potential of the solid grains in OC suspensions has been measured with Zeta-meter 3 device.

The operational principle of the device is based on the method of microelectrophoresis and it takes into consideration the migration speed of the particles taking place in the suspension environment within a capillary in the electrical area. Leica optical light microscope (OM) connected to the computer hardware has been used for the purpose of determining the porous and hollow structure of the ROC composite samples and the microscope images of all the samples have been captured. The metallographic samples of the ROC composites have been examined under 10 kV with FEI-INSPECT S50 device after coating with Pd-Au mixture. Microhardness measurements have been conducted with Vickers stinging tip on the metallographic samples. Microhardness measurements have been conducted under 10 g loads in Wolpert Vickers microhardness device. Hardness values have been detected by taking the average of at least ten measurements and standard deviations have been calculated.

III. Results and Discussion

XRD diffractogram of the OC samples synthesized in MMT and different initial CTAB concentrations are given in Fig. 2 and the results belonging to the initial CTAB concentration change of the distance among the OC layers are given in Table 3. As it could be seen from Figure 2; the peak seen at 2θ = 7,19º for pure clay is the characteristic peak of MMT. It is known that d distance is approximately 1,25 nm when he changeable basic cation is Na^+ in MMT [12[DFM2]]. d distance of the clay used in this study has been calculated as 1,23 nm. It is known that the distance between layers increase and the diffraction peak slides to lower degrees (to left) together with the modification of the MMT [13-15[DFM3]]. The increase in the basal distance between the OC layers after modification with CTAB shows that CTA^+ ions have placed in the basal spaces of the OC layers [16[DFM4]]. The basal spacing increase was found greater for OC-80, OC120 and OC-280 than other OC. XRD and zeta potential measurements indicated that interactions among MMT and CTA^+ ions interactions also caused an increase along interlayer spacing of OC structure [16[DFM5]].
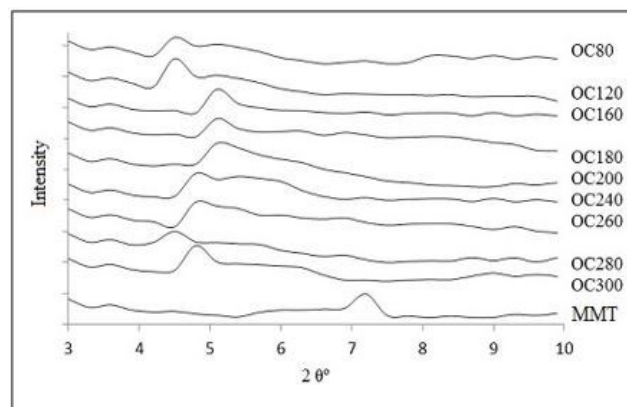

Fig. 2. XRD diffractograms MMT and OC.

Table 3. d and 2θ values of the MMT and OC attained from the XRD analysis.

Samples	d (nm)	2θ(º)
MMT	1,23	7,19
OC80	1,83	4,81
OC120	1,84	4,78
OC160	1,66	5,31
OC180	1,68	5,25
OC200	1,73	5,11
OC240	1,78	4,95
OC260	1,80	4,91
OC280	1,85	4,76
OC300	1,79	4,93

Microhardness values of the ROC composites are given in Table 4 and they have been shown in graphics against initial CTAB concentration in Fig. 3. The OM images of the ROC composites have also been taken for the purpose of being able to conduct an assessment on the surface morphologies of the synthesized ROC composites and they are also shown in Fig. 4. As it could be seen from Fig. 3 and Table 4; the hardness values of ROC composites other than the ROC502 and ROC508 synthesized from the OC modified in 120 mg/L and 280 mg/L CTAB concentration decrease together with the increasing CTAB concentration. In the ROC502 composite synthesized with the use of the clay modified in 120 mg/L CTAB concentration; it is understood that the cross-linked polymer blocks and the hydrogen bonding among these blocks have occurred in a more efficient way. The homogeneity of the structure in the OM image belonging to the ROC502 composite supports this result. It has been reported by Choi and Chung [17[DFM6]] that a decrease has been observed in the mechanical properties together with the increasing OC ratio in the novalak resin/ organoclay composites and the improvement in the mechanical properties is dependent on the degree of the hydrogen bond interaction between the modifier and phenolic resin. This situation indicates that the sign and density of the surface load of the OC layers are ultimately efficient on the efficiencies of the layer-chain interactions. When the clay modified with higher CTAB concentration is used, the interaction between the OC layers and polymer chain blocks decreases in parallel to the decreasing negative surface load density. The hydrocarbon queue density increasing on the layer surfaces sterically prevents the interactions of hydrogen bonding between the OC layers and cross-linked polymer blocks and therefore, the chain conformation in accordance with the crystal formation changes. This situation explains the decrease in the hardness values of the ROC503-507 composites synthesized with the use of the clay modified in 160, 180, 200, 240 and 260 mg/L CTAB concentrations. It is seen in the OM image of the ROC506 composite synthesized with

the use of the clay modified in 240 mg/L CTAB concentration that fractures have occurred. It has also been understood that the interactions of hydrogen bonding among the cross-linked polymer blocks have been sterically prevented by the OC layers in the ROC507 composite prepared in 260 mg/L CTAB concentration. The conformational changes not in accordance with the crystal formation have been efficient in the increase in the fracture ratios. The hardness value measured for the ROC508 composite synthesized with the use of the clay modified in 280 mg/L CTAB concentration is higher when compared to the value measured for the RPR. This situation shows that the cross-linked polymer blocks have leaned towards the OC layers bearing highly positive loaded centers and the crystal structure has occurred in micelle folding shape which is considered to have been established with the hydrogen bonding. It is seen from Table 4 that the ROC509 composite synthesized in 300 mg/L CTAB concentration has the lowest hardness value. It is clear in ROC509 composite that the interaction of the highly positive loaded OC layers with the cross-linked blocks and branched polymer chain has been realized upon the polarization with π electrons of the benzene rings. This situation has revealed a brittle polymer matrix.

Table 4. The microhardness values of the RPR and the ROC composites.

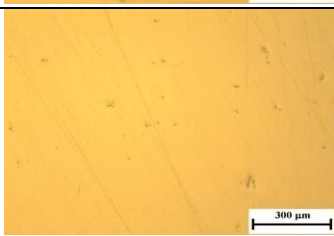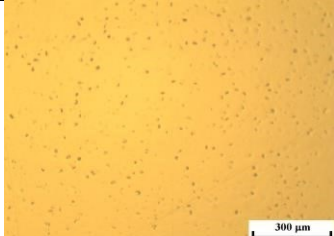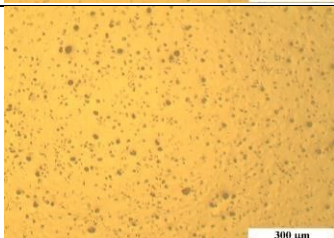| Samples	Microhardness (HV$_{0,01}$)
RPR	15.9
ROC501	14.9
ROC502	19.3
ROC503	14.4
ROC504	11.3
ROC505	13.3
ROC506	13.7
ROC507	12.6
ROC508	17.1
ROC509	3.36
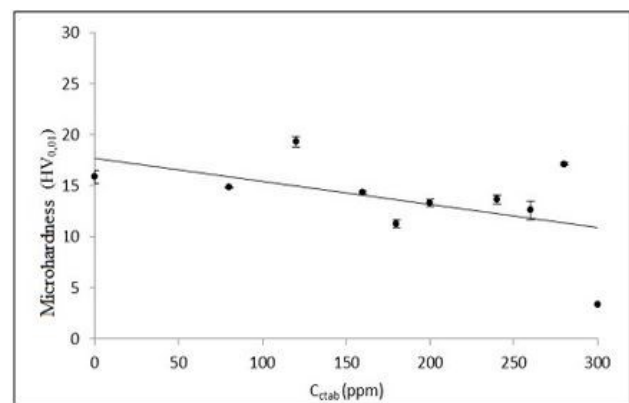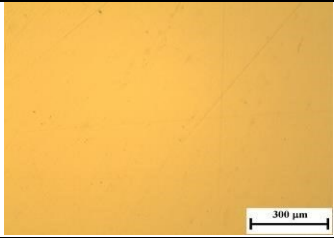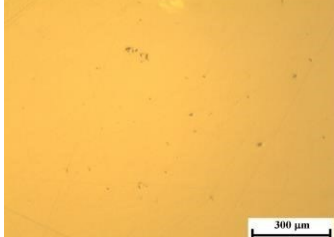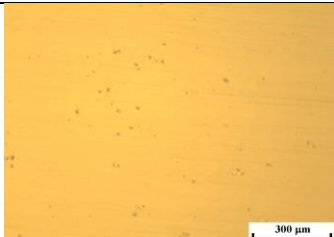
Fig. 3. Change of the microhardness values of the ROC composites with different initial CTAB concentrations.

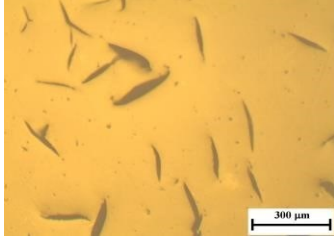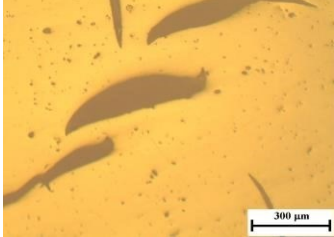| Composites	Optical microscope image (300μm)
ROC501	
ROC502	
ROC503	
ROC504	
ROC505	
ROC506	
ROC507	

ROC508	
ROC509	

Fig. 4. Optical microscope images of the ROC composites synthesized with the use of the OC prepared in different initial CTAB concentrations.

IV. CONCLUSION

The ROC composites (by the ratio of 1% in weight) prepared in different initial CTAB concentrations of OC and RPR with the ratio of 1,3 F/P and at 50ºC preliminary polymerization temperature and the ROC composites have been synthesized with in-situ polymerization technique. The results attained from the study could be summarized as follows.

- It has been determined that the pure clay samples are mainly in Na-MMT structure.
- It has been determined that CTAB which is used in different initial concentrations for the purpose of changing the surface charge sign and density of the clay layers and in this way, turning the clay into OC is effective in the surface charge density and in changing the basal distance between the layers.
- Zeta potential values of the MMT and OC samples have been measured and it has been observed that the zeta potential values of the samples have slid towards highly positive values when compared to those of the MMT in parallel to the increasing CTAB concentration.
- The hardness values of ROC composites except for the ones synthesized from the organoclay modified at 120 mg/L and 280 mg/L CTAB concentration have decreased together with the increasing CTAB concentration. This situation has revealed the fact that the hydrogen bond between the RPR and the OC synthesized in these concentrations is more efficient when compared to that of other ROC composites.
- ROC502 and ROC508 had the highest hardness values because they contained OC-120 and OC-280 respectively, and this OC samples showed the largest basal spacing.
- OM image of ROC502 composite represented more homogeneous surface than surfaces of other composites and had the highest hardness value.

- As a result, when the surface charges, basal spaces and microhardness values of ROC composites were compared, it was deduced that interactions among RPR chains and OC samples were fairly different.

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