Asian Journal of Chemistry Vol. 22, No. 1 (2010), 797-807

Preparation and Morphological Study of Epoxy/Silane Modified Nanoclay Nanocomposites

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Epoxy-clay nanocomposites were prepared using silane modified montmorillonite. The clay was first purified using a 1-inch hydrocyclon apparatus. The purified clay was modified with various amounts of (γ)-3-aminopropyltrimethoxysilane as a modifier. The synthesized organoclay was mixed and swollen by a mixture of epoxy resin and stoichiometric amount of curing agent at different temperature, mixing time and agitation. Finally, the compounds were cured in an oven at 90 ºC for 2 h. The nanostructure materials were characterized using X-ray diffraction and transmission electron microscopy. The X-ray diffraction patterns showed that the impurities and large particles (greater than 5 microns) are removed from the samples. The results showed that interlayer spacing was increased with increasing the amount of modifier and the basal distance in the organoclay was more than 2.1 nm which was larger than that of the original clay (1.24 nm). The X-ray diffraction patterns showed that the interlayer spacing of clay in the nanocomposite was increased and the 001 peak of the Montmorillonite was shifted to smaller 2 theta and in many cases disappeared. The X-ray diffraction and transmission electron microscopy results demonstrated that the layers of clay in the nanocomposite samples were fully exfoliated.

Key Words: Organoclay, Nanocomposite, Modification, Morphology, Exfoliation.

INTRODUCTION

In the nano science field, many researches have been conducted in nano-composite materials in two aspects science and industry point of view. Nanocomposites are made by dispersion of particles in nano scale in a matrix. The matrix could be metal, ceramic or polymer. The shape of particles could be spherical, fiber and flake or any desired shape.

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Epoxy resins, as an important class of polymers have many applications in different industries. Printing circuits of electronic parts, coating, vehicle manufacturing and aircraft industries as well as a part of composites in different industries are among the applications of epoxy resins. Due to nature of its structure, it is strong and has high resistance against heat and chemicals. When nanoclay is added to the epoxy, the product is a nanocomposite with properties much better than pure epoxy[1]. Enhancement of properties is dependent on dispersion of organoclay in the matrix and morphology of clay in nanocomposites[1]. The results of previous studies have showed that mechanical properties of epoxy-nanoclay nanocomposite with intercalation and exfoliation structure are much higher than mechanical properties of pure epoxy[1-6]. The morphology of epoxy-clay nanocomposites has also been the subject of many studies[2-6]. As shown in Table-1, alkyl ammonium has been used for clay modification process, *i.e.*, the morphology has been intercalation with interlayer spacing of 6.79 nanometer. In all of these studies, intercalation process has been done with ion exchanging of the modifier such as alkyl ammonium ions instead of clay interlayer sodium cations. These studies[2-6] have shown that there are many hydroxyl polar groups on the surface and edges of nanoclay structure, which can be useful for modification process.

TABLE-1
EFFECTS OF CLAY TYPE AND MODIFIER IN INTERLAYER SPACING [Ref. 2-6]

Ref.	Nanoclay type	Modifier type	d-Spacing in modified nanoclay (nm)	d-Spacing in nanocomposite (nm)
2	Cloisite 30B	Methyl tallow *bis*-2-hydroxyethyl quatetnary ammonium	1.86	3.82
3	Nanomer 1.3E	Octadecyl amine	2.37	2.95
4	Cloisite 93A	Ternary ammonium	2.58	3.78
5	Kunipia F	Cetyltrimethyl ammonium	1.94	5.41
6	Sodium bentonite EXM757	Dimethylbenzyl octadecyl ammonium chloride	1.74	6.79

It seems reasonable to follow the same trend in synthesizing epoxy-nanoclay nanocomposite with different modified nanoclay. To proceed, first, the purified nanoclay was modified by using suitable modifier materials (silanes) and then it was added to the epoxy in definite amount and under suitable processing conditions[7]. The nanocomposite microstructures and formed phases were studied by transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques.

Due to the increase of interlayer spacing, the possibility of polymer chain penetration into clay layer was expected. As a result of that the interlayer spacing would be more than the space in intercalation nanoclay. The increase of the interlayer spacing continues as the polymer chains presents in the system. So, the morphologies would be one of these: either intercalation or intercalation and exfoliation or a full exfoliation, depending on the degree of penetration of polymer chains.

EXPERIMENTAL

Local sodium bentonite with a mesh size of 200 and a particle size that was less than 75 µ was used in this study. The bentonite was produced by a powder company (Poodrsazan, Tehran, Iran) and amended with the chemicals shown in Table-2. A suitable γ-3-aminopropyltrimethoxy silane obtained from Sigma Aldrich was used to modify the clay. An Oxford-ED2000 XRF was used for all chemical analyses.

TABLE-2
CHEMICAL COMPOUNDS OF BENTONITE CONSUMPTION
(RESULTS OF XRF TESTS)

Formula	L.O.I	Na_2O	MgO	Al_2O_3	SiO_2	SO_2	Cl	K_2O	CaO	TiO_2	Fe_2O_3	BaO
Conc. (%)	13.2	2.04	2.22	14.59	61.03	0.37	0.46	0.76	0.77	0.22	2.09	0.11

Following preparation and analysis of the raw materials, the clay was purified using a 2-inch Hydrocyclon apparatus. To accomplish this, a suspension of 3 percent clay in distilled water was prepared and then passed through the cyclone at a pressure of 1.5 Kg/cm^2. This resulted in the removal of impure and large particles. Montmorillonite particles with a diameter of less than 6 µ were then dried and used in the compatibility process. To ensure compatibility following the dispersion of clay in distilled water, a suspension comprised of 3 per cent solids was prepared and amended with 10, 20, 30, 40 or 50 % of the modifier materials 'silane'. The mixtures were then heated at 80 °C for 6 h, after which the products were washed with distilled water and dried. The distribution of clay particle sizes was measured before and after purification using a laser particle size analyzer (Fritsch, LPSA, Germany). In addition, clay particles in the colloid state were analyzed by SEM, (Model LEO 440, England). The intercalation of the samples was evaluated using an X-ray diffraction (XRD system, Brocker, Germany).

In this project, domestic modified sodium bentonite, along with γ-3-aminopropyl trimethoxysilane, made by Sigma Aldrich Company with molecular formula of $H_2N(CH_2)_3Si(OCH_3)_3$ and the resin diglycidyl ether of bisphenol A (DGEBA) with Epikote 828^{TM}, from Shell company with 184-190 g/mol mass and 12-14 Pa.s viscosity and 1.16Kg/L density were used[8,9]. The curing agent was cycloaliphatic amine under Epikure F205 trade mark, from Shell Company with 0.5-0.7 Pa.s viscosity and 1.04 kg/L density. It was applied as the curing agent and as well as hardener[10].

After clay purification, the epoxy-nanoclay nanocomposite was prepared based on *in situ* polymerization process. For this purpose, the modified nanoclay was added to the resin in different amounts and composition. Then, by adding the curing agent, the compound was cured in the specified temperature and time inside the baking drier. To study the effects of processing conditions and other parameters, two sets of samples were prepared as it has been shown in Table-3.

In the first set, the clay content was changed (1.5, 3, 4.5 and 7 % wt). In the second series, the mixing temperature was altered (25, 50 and 75 ºC) and finally the mixing time (1, 2 and 3 h) were changed.

TABLE-3
CLAY CONTENT AND CONDITIONS OF EPOXY-NANOCLAY NANOCOMPOSITE PREPARATION

Samples	Testing variable			
	Clay per cent (% wt)	Mixing temperature (ºC)	Mixing time (h)	Stirring (rpm)
E1	1.5	50	2	2000
E3	3.0	50	2	2000
E5	4.5	50	2	2000
E7	7.0	50	2	2000
E525	4.5	25	2	2000
E575	4.5	75	2	2000
E51	4.5	50	1	2000
E53	4.5	50	3	2000

The details of modification process have been reported earlier[7]. After modification of montmorillonite by optimal per cent of silane (40 wt %) and achieving 20.43 Å interlayer spacing, it was added to epoxy resin in different percentages and the mixing took place in various processing conditions. After fully dispersion of the silicate layers inside the resin, the curing agent was added to the compound and the samples were cured inside driers at 90 ºC for 2 h. DSC (Model PL, made in England) was used for suitable temperature and suitable time determination for curing process of nanocomposite. Due to the applied resin nature (Epikoat 828), cycloaliphatic was chosen as curing agent. Curing agent to resin ratio was in the stoichiometric proportion (56 %). This process was performed with different percentages, (1.5, 3 and 4.5 wt %) of modified nanoclay.

The behaviour and intercalation of layers in the resin was studied with XRD (model Seisert-3003 PTS, made in Germany) and TEM (Model Philips-EM 208, made in Holland, 100 KV, $\Delta R = 3.5$ Å, step sizes = 1). Ultramicrotom (Model OMU3-C. Reichert, made in Austria) was also used for providing thin film (30-50 nm) of nanocomposite for TEM studies.

RESULTS AND DISCUSSION

In the modification process, named intercalation, as the organic compatibility materials is laid between clay layers, the interlayer spacing shows significant increase and the 001 peak shifts to smaller 2θ[1-8]. One of the most important methods of studying the changes of interlayer spacing is XRD technique. The displacement of 001 peak relevant to montmorillonite minerals, towards smaller 2θ angles could be used as a criterion for the changes of interlayer spacing. The XRD pattern of the purified nanoclay samples (modified and unmodified samples) in 2θ range between 2 to 10 are shown in Fig. 1.

The result of this study showed that domestic clay by applying a suitable purification and modification process can be used in the formulation of nanocomposites. Size distribution of purified samples showed that all particles higher than 5 μ were separated.

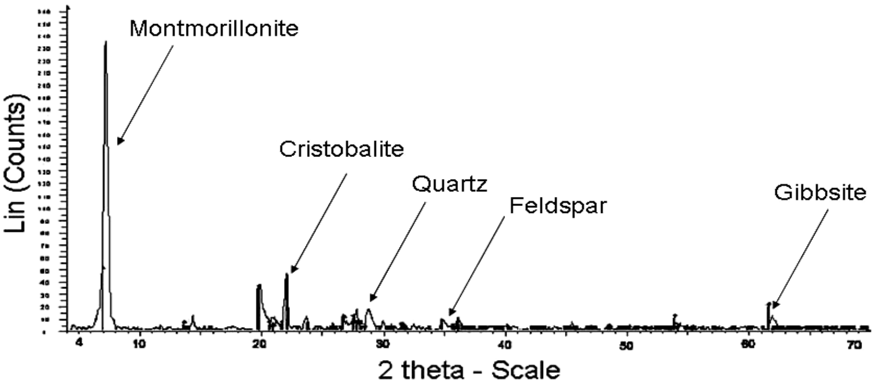

Fig. 1. XRD spectrum, local pure sample

Based on Fig. 2, it was shown that interlayer spacing of 12.43 Å in unmodified sample was increased to 20.43 Å after modification. As it has been mentioned in the literature, the replacement of Mg for Al in montmorillonite induces negative load in crystal which can be neutralized with sodium ions or similar ions in nature[11]. The number of positive ions in the structure of this mineral affects its properties particularly the ionic exchange degree with polymers in the modification and compatibility process. As it is shown in the modification process, the organic compounds are placed between clay layers and the interlayer spacing was increased as the effect of this process.

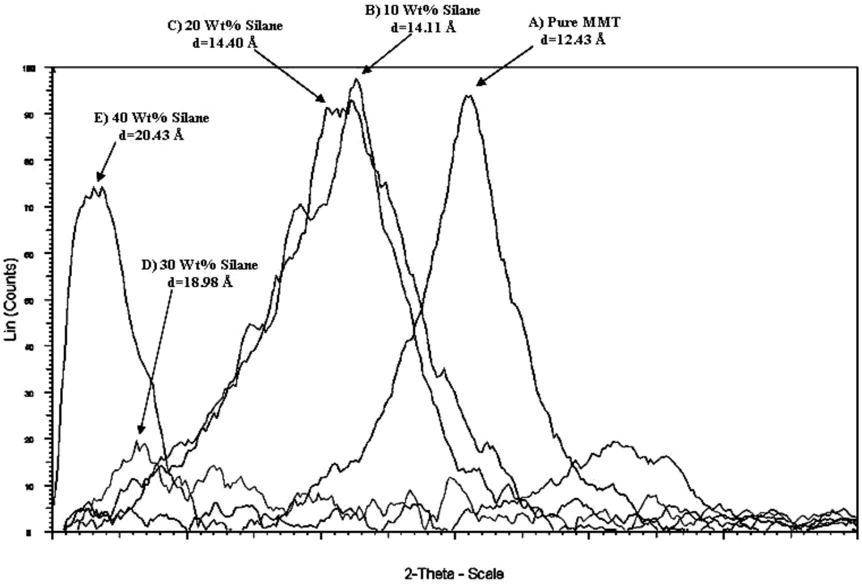

Fig. 2. (A) XRD spectrum of purified sample, (B) The sample modified with 10 wt % silane (C) The sample modified with 20 wt % silane (D) The sample modified with 30 wt % silane (E) the sample modified with 40 wt % silane

Forty per cent weight silane was selected as the optimal percent for modifier material in modification process.

The XRD spectrum of the purified and modified samples at 2θ between 4 and 10 ° is shown in Fig. 2. Fig. 2-A clearly indicates that the strong peak corresponding to the 001 montmorillonite mineral in the 2θ position is *ca.* 7 ° while, the interlayer spacing in the unmodified clay is *ca.* 12.5 Å[12]. As was expected, this value varied and increased as modifiers were placed between the layers. This effect shows that the increase in interlayer spacing is highly dependant on the amount of modifier used. As shown in the XRD spectra of the modified clay samples (Fig. 2B-E), increasing the amount of modifier from 10 to 40 % resulted in increased spacing of the interlayers. However, when the modifier amount was increased from 40 to 50 %, little additional increase in spacing was observed. This indicates that the interlayer spacing increased from 12.43 to 20.43 Å in response to modification. Based on these results, 40 wt % silane was selected as the optimum amount of filler for the modification process (Fig. 3).

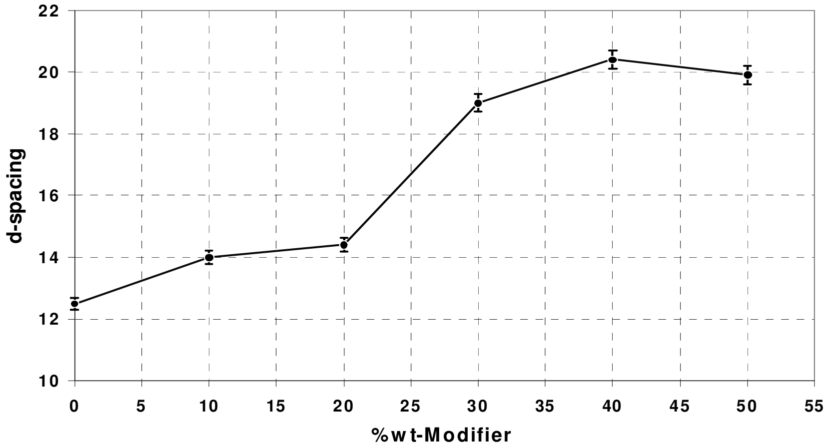

Fig. 3. Diagram of changes interlayer spacing by increase in the percent of modifier

It can be seen from XRD spectrum of the unmodified clay, the strong 001 peak of montmorillonite mineral is appeared at 2θ about 7 ° indications that the interlayer spacing is 12.43 Å. It seems that due to absence of positive ions in their structures, it is expected to have penetration of silane molecules in to the system and their absorption on the clay edges. As results, their condensation reaction would cause increase in the interlayer spacing. Such observation was in agreement with He *et al.*[8].

Fig. 4 shows the results of XRD patterns of the first set of samples (Table-3). As can be seen no peak was observed related to the crystal structure of montmorillonite, it is revealed that the clay structure is probably exfoliated. Such observation indicates that the interlayer spacing has been changed from 2.04 nanometer to more than 8.8 nanometer for the modified sample in nanocomposite and the full exfoliation structure, respectively. It is necessary to mention that, the ultimate limit for full exfoliation of clay layers was expected to be 8.8 nanometer[13]. The XRD results of epoxy-silane modified nanoclay nanocomposite evidenced by transmission electron microscopy.

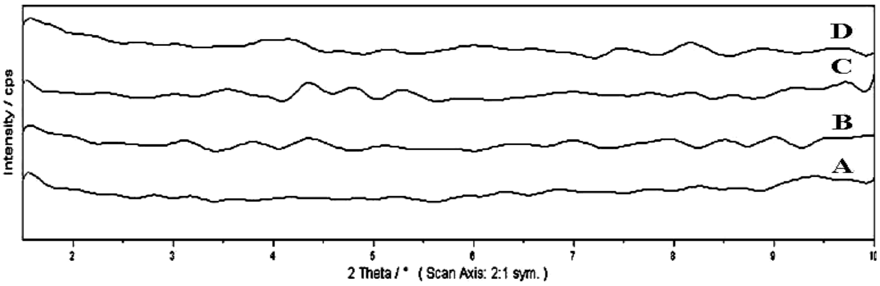

Fig. 4. XRD patterns of epoxy nanocomposite at different percentages of nanoclay (A) E-1.5 wt % nanoclay (B) E-3 wt % nanoclay (C) E-4.5 wt% nanoclay (D) E-7 wt% nanoclay

Transition electron microscopy (TEM) images showed a significant increase in montmorillonite interlayer spacing (Fig. 5). The TEM photomicrographs show that the small clay aggregates is well dispersed within the resin matrix. It must be noted that the dark spots in TEM images is related to the clay layers with higher density. As it has been mentioned in other's works, if the layers are not completely opened, they are shown as parallel black lines on the TEM image. The TEM images (Fig. 5A-C) indicated that interlayer spacing of clay has exceeded 10 nm that is more than the limit reported for layers exfoliation.

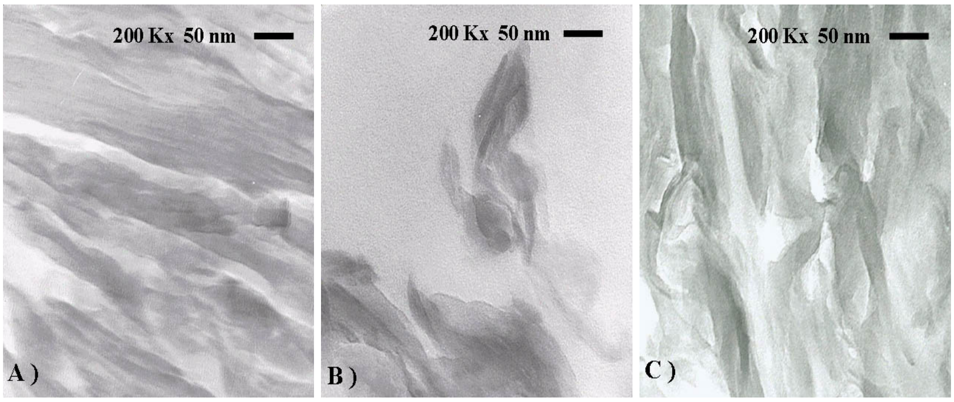

Fig. 5. TEM images of nanocomposite with different percent of modified nanoclay (A) 1.5 wt % (B) 3 wt % (C) 4.5 wt%

Transition electron microscopy (TEM) images of fully dispersed clay layers in laying form within the epoxy in nanocomposite samples with 1.5 and 3.0 wt % of modified nanoclay are presented in Fig. 5A and B. In addition, the existence of order exfoliated clay layers is observable shown in this TEM image. This shows that despite increase in the interlayer spacing, the accumulating structure of clay is not entirely destroyed. Increase in accumulating structure is obvious of the sample with 4.5 wt % modified nanoclay along with the exfoliation of clay layers inside the accumulation is obviously shown in Fig. 5C. These observations are in full agreement with the results obtained from XRD technique.

The mains reason for obtaining a fully exfoliated structure might be explained by the tendency of polymer chains penetration inside the montmorillonite layers. Beside, the thermodynamic trend of polymer chains which has been noted as a driving force for the penetration of chains into montmorillonite interlayer[14]. However, there are other factors which must be considered, *i.e.*, in the case of modified epoxy-nanoclay nanocomposite with silane, in addition to the thermodynamic trend, the chemical reactions between the amine-groups of silane modifier and the epoxy group become another factor that establishes a strong driving force for performing the intercalation process and exfoliation of the clay layers. The XRD results spectrum in Fig. 2 might be considered as a confirmation for this idea. These results show that the interlayer spacing of montmorillonite increases as a result of silane modifier reaction with the hydroxyl groups (Si-OH) on the edges as well as on the surface of clay layers.

It seems that the position of silane modifier between clay layers and the subsequent chemical reaction makes much stronger driving force to drag the polymer chains into the interlayer spacing and consequently, the space between layers is increased. The XRD spectra of different clay percent and TEM images showed in Fig. 5 indicate that regardless of the clay percentage, the morphology is of fully exfoliated. This is in contrary to the results obtained in nanocomposite with modified nanoclay by using alkyl ammonium[2-6]. In accordance with these observations, the following model has been proposed for the intercalation and exfoliation during the preparation of epoxy-clay nanocomposites filled with organosilane modified nanoclay (Fig. 6). Different steps have been considered in the proposed which are shown schematically in Fig. 7. We have modeled the formation of intercalated silane modified nanoclay as well as exfoliated epoxy-clay nanocomposites during the preparation of epoxy-clay nanocomposites filled with organosilane modified nanoclay as illustrated in Fig. 6. As previously mentioned and showed in the figure (step 1 and 2) intercalation process with silane modification took place as a result of silane modifier reaction with the hydroxyl groups (Si-OH) on the edges as well as on the surface of clay layers.

It seems that the position of silane modifier between clay layers and the subsequent chemical reaction makes much stronger driving force to drag the polymer chains into the interlayer spacing and consequently, the space between layers is increased. It must be noted that according to the XRD spectra and corresponding TEM images (Figs. 4 and 5) regardless of clay percentage the morphology in the experienced range is of fully exfoliation.

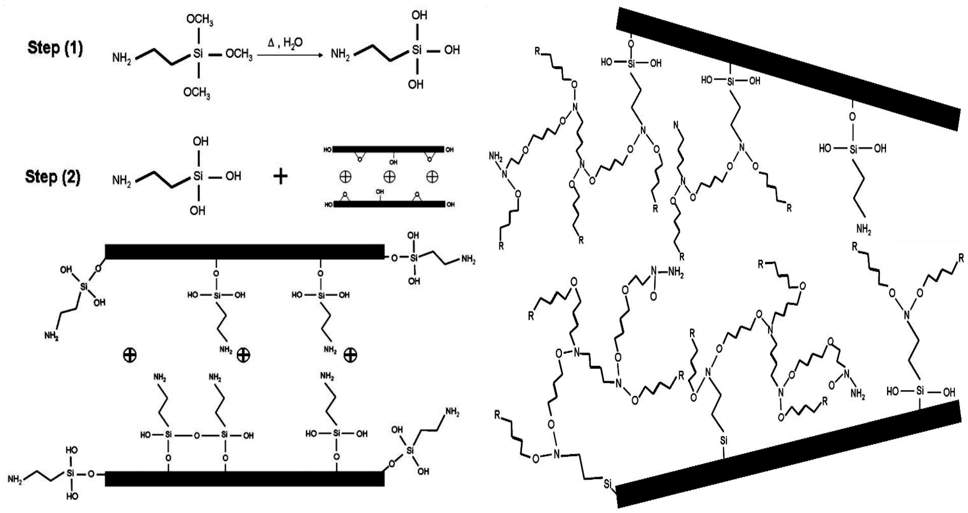

Fig. 6. Proposed schematic representation for the formation of epoxy-organosilane based nanocomposites

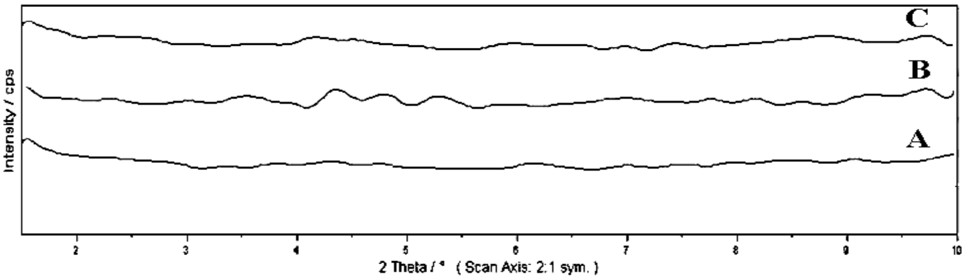

Fig. 7. XRD patterns of epoxy nanocomposite with 4.5 wt % modified nanoclay at: (A) 25 °C, (B) 50 °C and (C) 75 °C

As explained in previous sections, the TEM images and XRD spectra of samples of epoxy-nanoclay nanocomposite showed that montmorillonite modified with silane in the resin matrix has mainly exfoliated structure and in some area is in the accumulated form. Since the tests were carried out at 50 °C, the reaction between amine (NH_2) and epoxy resin could be a driving factor in dragging epoxy resin inside the clay layers. To study the effects of mixing temperature as well as specifying the minimum mixing temperature. Samples of nanocomposite with 4.5 wt. % nanoclay were prepared at different temperature, 25, 50 and 75 °C, respectively and the curing reaction was conducted in a stoichiometric ratio.

The XRD patterns prepared of nanocomposites with 4.5 wt. % modified nanoclay at different temperatures are shown in Fig. 7. It shows no peak in the 2θ range less than 10° which indicated that the interlayer spacing has been increased and the structure is exfoliated in all three samples. It seems that the temperature dependence of the morphology of clay in resin matrix is not significant, unlike the observation for alkyl ammonium[6,15]. This might be attributed to the high mobility of polymer chains, the modifier substance and activation of the reaction between silane modifier and epoxy resin in the thermal range subject of test.

In order to study the mixing time of epoxy resin and nanoclay, the testing time was taken in 1, 2 and 3 h at 50 °C. The XRD results are presented in Fig. 8. No peaks were detected for montmorillonite in the 2θ range (0-10°). thus, it may be inferred that the clay structure is completely exfoliated and the mixing time had no effect on the type of structure in this range.

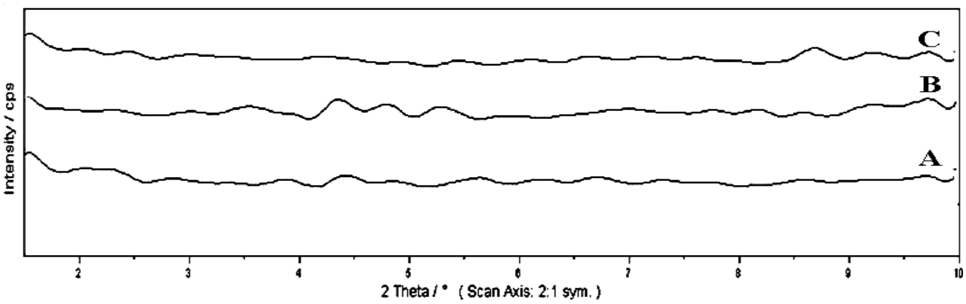

Fig. 8. XRD patterns of epoxy nanocomposite with 4.5 wt % modified nanoclay in times: (A) 1 h, (B) 2 h and (C) 3 h

As it was mentioned earlier, despite the pervious reports[16,17], the results obtained here showed that an increase in mixing time more than 1 h did not effect significantly on the intercalation of polymer chains into the clay layers.

Tak-Keun *et al.*[14] reported that the interlayer spacing increases with rotation speed of stirrer during the mixing but the morphology still is intercalated. Such results along with the results obtained on the effect of mixing time, temperature and nanoclay content indicate that the mechanism of intercalation of nanocomposite with silane differs from alkyl-ammonium. Based on these results, it is expected that the amino groups in the silane modifiers have significant role in making exfoliated nanoclay in resin matrix.

Conclusion

(a) The results showed that exfoliation of clay layers the role of modifier substance and the type of clay is more pronounce. (b) The results showed that an increase in the clay contents from 1.5 to 7 wt. %, the structure of nanocomposite was completely exfoliated and the interlayer spacing in clay layers was reached more than 8.8 nm. (c) The TEM results showed that as the aggregation of layers increases, the clay percentage grows up. (d) The results of XRD showed that the increase in temperature had no effects in nanocomposite morphology and mixing time more than 1 h has practically no effects on the structure. (e) The exfoliated structure was obtained in mixing times less than 1 h. (f) The results showed that at stirring rotation of 100 rpm, the morphology was completely exfoliated.

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(*Received*: 30 June 2009; *Accepted*: 16 September 2009) AJC-7904