

Polycondensation of ϵ -Caprolactone in the Layer Spaces of Organophilic Montmorillonite and Its Characterization

Sung-Jun Cho[†]

Division for New Materials Engineering, Paichai University, Daejeon 302-735, Korea
(Received March 3, 2005; Accepted March 30, 2005)

ABSTRACT

The polymerization of ϵ -caprolactone in the layers of the [DEACOOH]-Montmorillonite intercalations complex was attempted using 10-Carboxy-n-decyldimethylethylammonium bromide and Na-Montmorillonite to achieve [DEACOOH]-Polycaprolactone-Montmorillonite in which the inorganic material (montmorillonite) and the organic material (polycaprolactone) are chemically linked each other. The results of X-ray- and IR-analysis for the samples obtained after polymerization showed that the polymerization reaction has been successfully accomplished. In order to study the polymeric reaction products more precisely we have separated the polymerized product from the silicate layers and analyzed it with X-ray diffractometer, IR-spectrometer and TEM. The comparison of the results of X-ray- and IR-analysis for the separated polymer with them for the polymer which was synthesized by the reaction of ϵ -caprolactone only with the organic cation without montmorillonite showed that the obtained both polymers are the same compounds.

Key words : ϵ -caprolactone, Nanocomposites, Inorganic material, Organic material

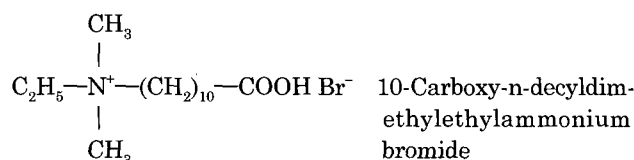
1. Introduction

Clay has a very small particle size, exists abundantly in the nature and is very useful material in the economic and environmental aspects. It has also excellent mechanical and chemical properties and so has been broadly used as a reinforcement for polymers. To improve the chemical, physical, mechanical, electrical and thermal properties such as chemical resistance, strength, toughness, stiffness, elasticity, isolation, etc. of the pure polymer materials without reinforcement or filler the study on the synthesis of the clay-polymer nanocomposites by reinforcing this pure polymer materials with clay minerals as a reinforcement has been very active.¹⁻⁴⁾ Theoretically it is possible to form inorganic-organic complexes in which both, inorganic material (for example; inorganic montmorillonite) and organic material, are chemically combined, and the studies on this research area are also very active.⁵⁻¹³⁾

Poly(ϵ -caprolactone)(PCL) is a kind of biodegradable aliphatic polymer and is recently being much researched for use in pharmaceutical controlled release systems, medical devices and in degradable packaging.¹⁴⁻¹⁶⁾ Especially PCL has a very excellent commercial use as a copolymer with polyvinylchloride, acrylonitrile-butadiene-styrene, etc.¹⁷⁻²⁰⁾ But the future development for the potential use of this PCL is much limited, because it has a low melting point and

glass transition temperature(Tg). Therefore it could be applied in the various fields, if its mechanical properties can be improved by reinforcing it with reinforcements or fillers such as clay.

Clay becomes fully other properties, if the metal cations in the interlayer spaces of clay will be substituted by other cations, especially by organic cations. It means that the properties of clay can be fully changed by the kind of the organic cations which will be intercalated between the layers of clay. For example Giannelis²¹⁾ and Wei²²⁾ used 11-carboxy-undecylammonium chloride as an organic cation formed from 12-aminolauric acid and concentrated HCl to synthesize PCL/Clay Nanocomposites. Octadecylammonium chloride was used as an organic cation in the synthesis of epoxy-clay nanocomposites by Berglund.²³⁾ In this research we have used the following quaternary ammonium salt as an organic cation with long alkyl chain synthesized by the method described in earlier publication.²⁴⁾



(will be abbreviated as [DEACOOH] Br after now)

In other researches the Organically Modified Montmorillonite(OMM) was synthesized by a cation exchange reaction between Na-montmorillonite and primary ammonium salt

[†]Corresponding author : Sung-Jun Cho

E-mail : sjcho@mail.paichai.ac.kr

Tel : +82-42-520-5394 Fax : +82-42-520-5394

which was prepared in situ from aminolauric acid and concentrated HCL in distilled water.^{25,26} Thereafter the poly(ϵ -caprolactone)-montmorillonite nanocomposite(PCLM) was synthesized from OMM and ϵ -caprolactone in a vaial at 170°C(oil bath temperature). But in this research the quaternary ammonium salt as an organic cation was prepared at first, whereafter the OMM was formed by a cation exchange reaction between Na-montmorillonite and this quaternary ammonium salt. And then the OMM was treated with ϵ -caprolactone to obtain organic cation- ϵ -caprolactone-montmorillonite intercalations complex(OCM), whereafter this OCM was heated at various higher temperature than 170°C in a sealed evacuated ampule for the polymerization reaction to obtain PCLM.

2. Experimental Procedure

2.1. Materials

n-undecanoic acid bromide and dimethylethylamine for the preparation for the organic cation and ϵ -caprolactone as starting material for the organic polymer were commercially obtained from Fluka and/or Aldrich. Ca-bentonite from Schwaiba, Germany was chemically refined to achieve Na-Montmorillonite.

2.2. Characterization of Synthesized Products

The obtained organophilic [DEACOOH]-Mont intercalations complex, [DEACOOH]- ϵ -caprolactone-Montmorillonite, [DEACOOH]-polycaprolactone-Montmorillonite and the separated samples treated with the $\text{NH}_4[\text{HF}_2]$ -solution were characterized by X-ray diffractometer (Philips Novelco and XPERT PRO) using Cu $K\alpha$ -radiation ($\lambda = 1.5418 \text{ \AA}$) with a scan speed of 1.00 deg/min.

Infrared spectroscopic measurements on the pure Na-Montmorillonite, the organophilic [DEACOOH]-Mont intercalations complex, [DEACOOH]-polycaprolactam-Montmorillonite, the polymer material separated from this inorganic/organic hybrid and the pure polymer synthesized without montmorillonite were also performed using FT-IR-spectrometer(BOMEM MB-104).

The synthesized montmorillonite/polycaprolactone nanocomposites were also analyzed with transmission electronic microscopy(TEM; JEOL 100 LX with 100 kV Accelerating Voltage).

2.3. Synthesis of the Organophilic [DEACOOH]-Mont Intercalations Complex

[DEACOOH] Br was dissolved in distilled water and this solution was added to the water suspension of Na-Montmorillonite under stirring. The whole mixture was then left at 65°C for 48 h under occasional stirring and thereafter centrifuged so that the swelling solution can be isolated from the product, the organophilic [DEACOOH]-Mont intercalations complex. This [DEACOOH]-Mont was washed with dist. water and then dried at 100°C in oven at first and continuously at 65°C in vacuum of 10^{-3} torr for 24 h.

2.4. Synthesis of [DEACOOH]- ϵ -Caprolactone-Montmorillonite

In the 100 mL round flask the stoichiometrical amounts of the organophilic [DEACOOH]-Mont and ϵ -caprolactone were well mixed with mortar, and then the mixture was left under N_2 -atmosphere for 30 min under occasional stirring. Thereafter the round flask with the mixture was heated at 95°C(oil bath) for 30 min, cooled slowly up to 50°C, and well mixed with mortar. Then the sample was put into the reaction flask again, left under N_2 -atmosphere for 30 min with occasional stirring, heated at 95°C for 30 min, cooled slowly up to 50°C and left at this temperature for 3 days. This procedure was repeated 3 times more.

2.5. Polyconsation of ϵ -Caprolactone between the Layers of [DEACOOH]-Mont

[DEACOOH]- ϵ -caprolactone-Montmorillonite was put into the thick horosilicate ampule which was preheated with heat gun to remove the moisture, and then the ampule (including sample) was evacuated, sealed and heated at 220°C, 230°C, and 240°C for 48 h to polymerize the ϵ -caprolactone in the interlamellar spaces of [DEACOOH]-Mont.

2.6. Polycondensation of ϵ -Caprolactone and [DEACOOH] Br without Montmorillonite

In order to compare with the polymer obtained from the above procedure the organic monomer, ϵ -caprolactone, alone was polymerized with the organic cation, [DEACOOH] Br without montmorillonite at 240°C for 48 h. The product was purified by washing with water and drying at 65°C for 24 h in high vacuum of 10^{-3} torr.

2.7. Separation of Polycaprolactone from the Layers of [DEACOOH]-Mont

The polycaprolactone polymerized in the layers of the organophilic [DEACOOH]-Mont intercalations complex was separated by the decomposition of silicate lattice using an ammonium hydrogen fluoride($\text{NH}_4[\text{HF}_2]$) solution. The pure Na-Montmorillonite which wasn't polymerized, i.e. don't include any organic compound was also decomposed in the same way for the purpose of comparison.

Polycaprolactone- and Na-Montmorillonite were mixed with excess amount of 1 n solution of ammonium hydrogen fluoride, respectively. Each mixture solution was then left at room temperature for 2 days under stirring, and thereafter conc. ammonium hydroxide(NH_4OH) solution was added to each one which had a pH 3.5 at the beginning so much that it will be neutral or weak alkalic. The precipitate was separated from the solution by the filtration, dried at 65°C for short time in oven at first and then continuously in high vacuum of 10^{-3} torr for 24 h. This dried sample was mixed with the excess amount of 100% glacial acetic acid, and the mixture was filtered at 60~70°C. The separated glacial acetic acid phase was then treated with an excess of diethyl ether for the precipitation. The polymer precipitate was then separated and dried at 65°C for 24 h in high vacuum (10^{-3} torr).

3. Results and Discussion

3.1. Organophilic [DEACOOH]-Mont Intercalation Complex

The organophilic [DEACOOH]-Mont intercalations complex obtained from the reaction between Na-Montmorillonite and [DEACOOH] Br by the cation exchange reaction was characterized with an X-ray diffractometer under the following conditions:

- The equilibrium solution after cation exchange reaction was centrifuged; the solid residue was analyzed with X-ray diffractometer under still wet condition with the adherent equilibrium solution (Fig. 1(B)).
- Thereafter the centrifuged solid residue was washed eight times with distilled water until it was free from halide and characterized with X-ray diffractometer under still wet condition with water (Fig. 1(C)).
- The washed sample was dried at 65°C for 24 h in high vacuum (10^{-3} torr) and analyzed with X-ray diffractometer under the dried condition in high vacuum (Fig. 1(D)).

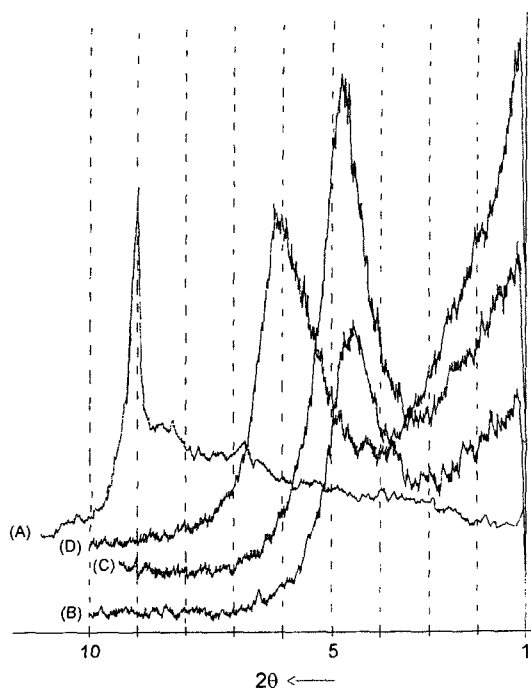


Fig. 1. X-ray diffraction patterns of [DEACOOH]-Mont. (A) Na-Montmorillonite dried in high vacuum at 65°C 24 h, (B) after 48 h exchange-time, under exchange solution, (C) after eight times washing, under water, and (D) after 24 h drying in high vacuum at 65°C.

The obtained results from the measurements with X-ray diffractometer are summarized in Table 1 which shows us that the basal spacing values between the starting material, Na-montmorillonite, and the reaction products, [DEACOOH]-Mont, are quite different. The Na-Montmorillonite used as a starting material swells toward infinitely under distilled water, *i.e.* the layers of the crystals separate to the individual layers. So the attractive interactions between the adjacent layers will reduce. After drying it under high vacuum its basal spacing falls to 9.8–10.1 Å. The X-Ray Diffraction (XRD) patterns for the summarized data in Table 1 are demonstrated in Fig. 1.

In case of [DEACOOH]-Mont the basal spacing of 19.6 Å is obtained under the exchange solution, but it lies on 18.5 Å with the reduction of 1.1 Å after washing eight times with water until it was free from halide. Under this condition it is obvious that the sample has still much water between the layer of the intercalations complex. Therefore the sample was dried at 65°C in high vacuum (10^{-3} torr) for 24 h, whereafter the closed packing was obtained and the basal spacing also decreased upto 14.50 Å with the reduction of 4 Å. It is a comprehensible value, because the density of charge of montmorillonite used in this research is very small. Under such density of charge the alkyl ammonium ions with up to at least 12 C-Atom numbers form a flat lying monolayer, as we know from many other researches.

Fig. 2 shows the XRD-patterns for the [DEACOOH]- ϵ -caprolactone-Montmorillonite synthesized by the reaction between the organophilic [DEACOOH]-Mont intercalations complex and ϵ -caprolactone. As showed in Fig. 2 the XRD pattern of the [DEACOOH]- ϵ -caprolactone-Montmorillonite is quite different from that of the starting material, the organophilic [DEACOOH]-Mont intercalations complex. This suggests that the caprolactone is successfully intercalated into the layer of [DEACOOH]-Mont. But from Fig. 2 we can see that the XRD patterns obtained after drying in high vacuum directly after the cation exchange reaction and after extraction with methanol and the following drying in high vacuum are almost the same as that of the starting material, the organophilic [DEACOOH]-Mont intercalations complex. This suggests that the intercalated ϵ -caprolactone between the layers of [DEACOOH]-Mont are extensively removed again from the layers.

3.2. Polycondensation Reaction

In order to know if the polymerization of ϵ -caprolactone in the layers of [DEACOOH]-Mont has been successful the sample was treated in high vacuum at 65°C for 24 h. Under

Table 1. Basal Spacings(Å) Measured After the Cation Exchange Reaction

Sample treatment	Basal spacing(Å) of	
	Reaction product	Na-Montmorillonite
after more than 48 h exchange time, under exchange solution	19.62	-
after eight times washing, measured under water	18.54	Toward infinitely
after 24 h drying in high vacuum at 65°C	14.54	9.8~10.1

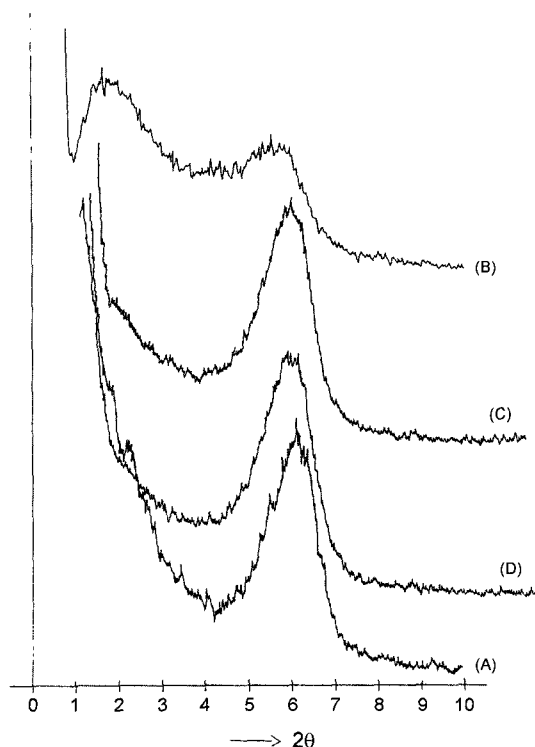


Fig. 2. X-ray diffraction patterns of [DEACOOH]-Mont with ϵ -caprolactone. (A) [DEACOOH]-Mont as a starting material, (B) after intercalation of ϵ -caprolactone into [DEACOOH]-Mont, (C) after drying of (B) in high vacuum right after the exchange reaction, and (D) after extraction with methanol and following drying in high vacuum of (B).

these conditions the unreacted ϵ -caprolactone which is only intercalated into the silicate layers will be removed from the layers again, and the basal spacing will be falling to ca. 14.5 Å which was the value for the starting material, [DEACOOH]-Mont dried in high vacuum. Independent of this procedure, the extraction analyses of samples were performed with the solvents in which only the monomer or small oligomers are soluble, but not the polymer. The results measured with X-ray diffractometer are showed in Table 2 and Fig. 3.

From the results of Table 2 and X-ray diffraction patterns in Fig. 2 we can see that ϵ -caprolactone was almost fully removed from the layers of [DEACOOH]-Mont, if the caprolactone was not polymerized in the layers, dried at 65°C for

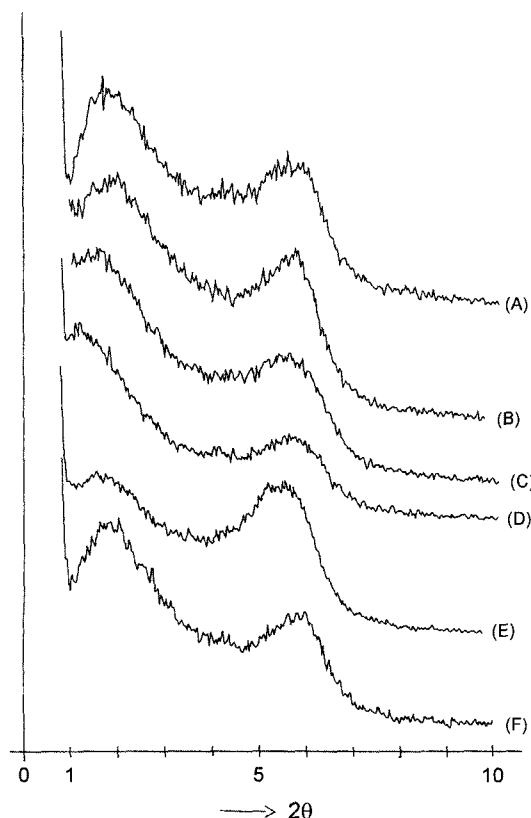


Fig. 3. X-ray diffraction patterns of [DEACOOH]-Mont with ϵ -caprolactone after polymerization. (A) [DEACOOH]- ϵ -caprolactone-Mont as a starting material, (B) after polymerization of (A) for 48 h at 220°C, (C) after polymerization of (A) for 48 h at 230°C, (D) after polymerization of (A) for 48 h at 240°C, (E) after drying in in high vacuum at 65°C 24 h of (D) right after polymerization, and (F) after extraction with methanol and following drying in high vacuum of (D).

24 h in high vacuum directly after intercalation reaction (Fig. 2(C)) and after extraction with solvent(here methanol for example) (Fig. 2(D)). But the results of Table 2 and Fig. 3 show us that the ϵ -caprolactone was not removed from the layers after the polymerization. This suggests that the polymerization of ϵ -caprolactone is successfully performed between the layers of [DEACOOH]-Mont.

In the second column of the Table 2 the basal spacings of the reaction products, [DEACOOH]-Caprolactone-Montmo-

Table 2. Results of Polymerization of ϵ -Caprolactone in [DEACOOH]-Mont.

Sample treatment	Basal spacings(Å) after reaction of [DEACOOH]-Mont. with monomer before polymerization	Basal spacings(Å) for 48 h at		
		220°C	230°C	240°C
starting material for polymerization	50.72			
after polymerization		49.74	57.53	68.83
dried in high vacuum at 65°C, 24 h	15.34	44.05	48.18	51.73
after extraction with methanol and dried in high vacuum at 65°C, 24 h	14.53	35.69	45.62	48.18

rillonites, which were synthesized by the intercalations reaction of ϵ -caprolactone into the [DEACOH]-Mont and will be used as a starting material for the polymerization of the organic monomer are summarized. The basal spacing of [DEACOOH]-Caprolactone-Montmorillonite before polymerization was 50.72 Å, but it was reduced to 15.34 Å after intercalation reaction and drying at 65°C, for 24 h in high vacuum. This is caused by the removal of almost all ϵ -caprolactone from the layers in high vacuum by vaporization. The Table 2 and Fig. 3 show us also that in case of the extraction with solvent, methanol, in which the monomer is soluble and the following drying in high vacuum at 65°C for 24 h the monomer, ϵ -caprolactone, was also removed from the layers and the basal spacings fell to 14.53 Å.

In the next column of the Table 2 the basal spacings of the products which were obtained after polymerization for 48 h at 220°C, 230°C, and 240°C are summarized. From the results of the Table 2 we can see that in every case the basal spacing increased with the reaction temperature. After polymerization at 220°C the basal spacing is 49.74 Å, while the basal spacings obtained after polymerization at 230°C and at 240°C are 57.53 Å and 68.83 Å, respectively. From these results it is obvious that the polymerization has been successfully proceeded and the reaction proceeds more rapidly in the higher reaction temperature.

We can observe more precisely the polymerizations state by checking the basal spacings measured directly after drying at 65°C for 24 h in high vacuum. The basal spacing of the sample synthesized after polymerization at 220°C is 49.74 Å, but it fell to 44.05 Å after drying at 65°C for 24 h in high vacuum. Therefore a large difference exists between the basal spacing between the two cases, from which we can know that large amounts of the monomer, ϵ -caprolactone, intercalated between the interlamellar space have been removed from the layers. The results obtained after polymerization for the reaction temperature of 230°C and 240°C are different from those at 220°C. For example the basal spacings measured after polymerization at 230°C and 240°C and directly after drying of these polymer products at 65°C for 24 h in high vacuum are 48.18 Å and 51.73 Å, respectively.

While the basal spacings obtained before polymerization lie between 14.53 Å because almost all amounts of the monomer were removed from the layers, those measured after extraction of the polymerized sample with solvent (here methanol) in which the monomer is soluble and the following drying at 65°C for 24 h in high vacuum are more than 35 Å in all cases, which means that the polymerization proceeded successfully. In general we can see from the results of the Table 2 that the less the basal spacing reduces the higher the reaction temperature is.

Comparing Figs. 2 and 3 it is obvious that the X-ray peaks obtained after polymerization are not sharp and far more broad than those measured before polymerization. For this reason the basal spacings for the X-ray patterns after polymerization are much less precise than those obtained before

polymerization. Therefore due to the difficulty in measuring the exact basal spacings from the X-ray peaks after polymerization, it has to be considered that only the rough basal spacings could be taken in Table 2 and that the limit of error is 3 Å or more.

3.3. Analysis of the Polymer Separated from the Layers

In order to more precisely investigate and analyze the polymer products the polymerized sample was isolated from the silicate layers. But as we know from the results of the extraction with solvent it was not possible to separate the polymerized product from the interlamellar space by extraction with solvent. It was also not possible to isolate the polymer ion existing between the layers by the cation exchange reaction because the ion with high molecular weight is linked more strongly with montmorillonite in the inter-

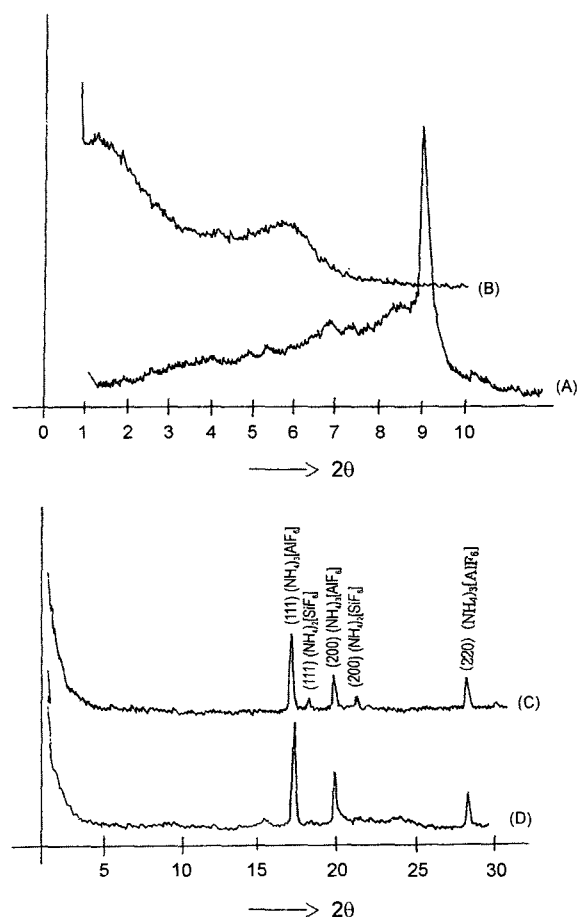


Fig. 4. X-ray diffraction patterns of (A) Na-Montmorillonite, dried in high vacuum at 65°C for 24 h, (B) [DEACOOH]-Polycaprolactam-Montmorillonite, polymerized for 48 h at 240°C, extracted with methanol and dried in high vacuum at 65°C for 24 h, (C) insoluble residue in water and $\text{NH}_4[\text{HF}_2]$ -water solution of Na-Montmorillonite after decomposition reaction, (D) insoluble residue in water and $\text{NH}_4[\text{HF}_2]$ -water solution of [DEACOOH]-Polycaprolactone-Montmorillonite after decomposition reaction.

lamellar space than the ion with low molecular weight. Therefore in order to separate it we had to decompose the silicate lattice with the $\text{NH}_4[\text{HF}_2]$ -solution. The isolated sample was then analyzed with X-ray diffractometer and IR-spectrometer, and the results are demonstrated in Figs. 4 and 5.

3.4. X-Ray Analysis After the Decomposition Reaction

The X-ray diffraction patterns before and after the decomposition reaction of Na-Montmorillonite and [DEACOOH]-Polycaprolactone-Montmorillonite are demonstrated in Fig. 4, from which we can observe that the decomposition reaction has been proceeded successfully, *i.e.* montmorillonite is decomposed by the chemical reaction with $\text{NH}_4[\text{HF}_2]$. From Fig. 4 we can see that the typical (001)-peaks for montmorillonite disappeared, while those peaks for the precipitates

which are not soluble in $\text{NH}_4[\text{HF}_2]$ -solution appeared; (111)-, (200)-, and (220)-peaks which are very sharp are related to the $(\text{NH}_4)_3[\text{AlF}_6]$ precipitate, while (111)- and (200)-peaks to

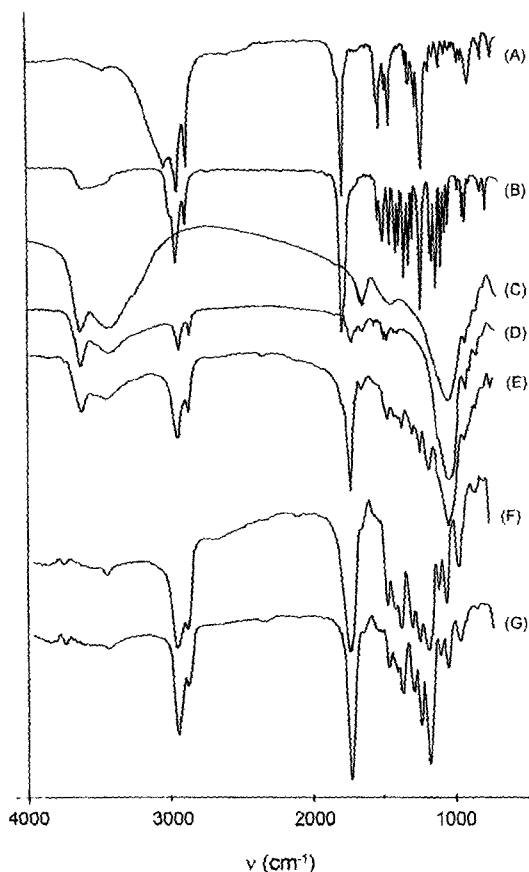


Fig. 5. IR-Spectrums for (A) [DEACOOH] Br, (B) ϵ -caprolactone, (C) Na-Montmorillonite, (D) [DEACOOH]-Montmorillonite, (E) [DEACOOH]-Polycaprolactam-Montmorillonite, polymerized for 48 h at 240°C, extraction with methanol and dried in high vacuum at 65°C for 24 h, (F) polymer, isolated from the interlayer space of montmorillonite (original polymerization in interlayer space at 240°C for 48 h, extracted with methanol, then isolated by $\text{NH}_4[\text{HF}_2]$ -process, and (G) polycaprolactone, synthesized without montmorillonite, after extracted with water and dried in high vacuum at 65°C for 24 h.

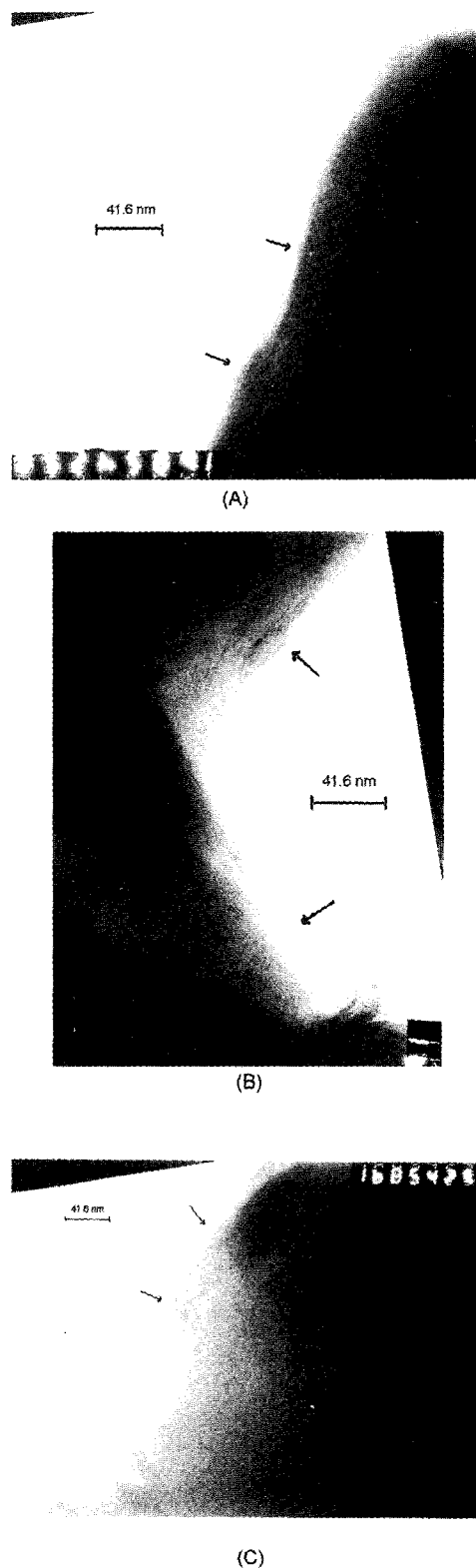


Fig. 6. TEM pictures of the montmorillonite/polycaprolactone nanocomposites at (A) 220°C, (B) 230°C, and (C) 240°C.

the $(\text{NH}_4)_2[\text{SiF}_6]$ precipitate. Here Al and Si from $[\text{AlF}_6]_3^-$ anion and $[\text{SiF}_6]_2^-$ anion, respectively, can be derived only from montmorillonite lattice layers.

3.5. IR-Analysis

The results of IR-analyses for each sample are showed in Fig. 5. The IR-spectrums for [DEACOOH] Br, ϵ -caprolactone and Na-Montmorillonite as starting materials are showed in Fig. 5(A), (B), and (C), respectively. The IR-spectrum for Na-Montmorillonite includes somewhat characteristic broad peaks. Fig. 5(D) shows us the IR-spectrum for [DEACOOH]-Mont with the cation in the interlamellar space. In this spectrum we can observe the sharp peaks in the region from 2828 to 2915 cm^{-1} , from 1470 – 1530 cm^{-1} and at 1750 cm^{-1} which did not exist in the spectrum for Na-Montmorillonite and are derived from the organic cation intercalated between the layers.

Fig. 5(E) shows the IR-spectrum for [DEACOOH]-Polycaprolactone-Montmorillonite sample synthesized by the polycondensation reaction of ϵ -caprolactone between the layers of [DEACOOH]-Mont intercalations complex, extracted with methanol solvent to remove the caprolactone which were not polymerized, and then dried at 65°C for 24 h in high vacuum. In this case we can observe additional sharp peaks.

In Fig. 5(F) the IR-spectrum for the sample isolated from the interlayer spaces of montmorillonite after decomposition of [DEACOOH]-Polycaprolactone-Montmorillonite with $\text{NH}_4[\text{HF}_2]$ was demonstrated. In order to compare it with the spectrum for the polymer which was synthesized by the reaction of ϵ -caprolactone with [DEACOOH]-Mont without montmorillonite is showed in Fig. 5(G). Compared Fig. 5(F) with Fig. 5(G) we can observe that the both polymers which were synthesized under the different reaction conditions are the same compounds.

It is obvious from the polymerization experiments and the results of IR-Spectrums (Fig. 5(E), (F), and (G)) that a chemical reaction (polymerization) in the interlamellar space of [DEACOOH]-Mont appeared.

3.6. Transmission Electronic Microscopy(TEM)

In order to observe the appearance of the clay mineral as a reinforcement in the polymerized product this polymer was investigated with transmission electronic microscope(Fig. 4). From Fig. 4 we can observe the repeating arrangement of the layers of the reinforced montmorillonite in the polymer matrix of montmorillonite/polycaprolactone nanocomposites.

4. Conclusions

In this research we have tried to polymerize ϵ -caprolactone in the interlamellar space of [DEACOOH]-Mont to achieve the [DEACOOH]-Polycaprolactone-Montmorillonite in which the inorganic material(montmorillonite) and the organic material(polycaprolactone) are chemically linked each other and have found the following results:

1. The basal spacings for the samples obtained after polymerization lie from 35.69 Å to 51.73 Å under dried condition in high vacuum, while those for the samples before polymerization lie between 14.53 Å and 15.34 Å under the same condition.

2. Especially we could observe that the less the basal spacing reduces the higher the reaction temperature is.

3. From the comparison between the IR-spectrum of the starting material before polymerization and that of the product obtained after polymerization we could see that the polymerization appeared in the interlamellar space of the intercalations complex.

4. Compared the IR-spectrum for the sample separated from the layers of [DEACOOH]-Mont after polymerization of ϵ -caprolactone between the layers of [DEACOOH]-Mont with that for the polymer synthesized by the reaction of ϵ -caprolactone only with the organic cation, [DEACOOH] Br, without montmorillonite it is obvious that the both polymers which were synthesized under the different reaction conditions are the same compounds.

5. The repeating arrangements of the layers of the reinforced montmorillonite in the polymer matrix of montmorillonite/polycaprolactone nanocomposites were also observed by TEM.

From all these results it appears that the polymerization was successfully accomplished in the interlamellar space of the [DEACOOH]-Mont intercalations complex.

REFERENCES

1. D.-I. Dominghaus H., "Zusatzstoffe für Kunststoffe, Zechner & Huthig Verlag GmbH," Speyer am Rhein, Germany, 114-20 (1978).
2. A. J. Dankwerth, *Kaolin Clay*, Modern Plastics Encyclopedia, Breskin & Charleton Pub. Corp., New York, 393-94 (1972/73).
3. J. H. Etlinger, *Glass*, Modern Plastics Encyclopedia, Breskin & Charleton Pub. Corp., New York, 393 (1972/73).
4. R. B. Seymour, *Fillers for Polymers*, Modern Plastics Encyclopedia, Breskin & Charleton Pub. Corp., New York, 382-88 (1972/73).
5. T. Lan and T. J. Pinnavaia, "Clay-Reinforced Epoxy Nanocomposites," *Chem. Mater.*, **6** 2216-19 (1994).
6. H. Shi, T. Lan, and T. J. Pinnavaia, "Interfacial Effects on the Reinforcement Properties of Polymer-Organoclay Nanocomposites," *Chem. Mater.*, **8** 1584-87 (1996).
7. R. A. Vala, K. D. Jandt, E. J. Kramer, and E. P. Giannelis, "Microstructural Evolution of Melt Intercalated Polymer-Organically Modified Layered Silicates Nanocomposites," *Chem. Mater.*, **8** 2628-35 (1996).
8. M. Laus, O. Francescangeli, and F. Sandrolini, "New Hybrid Nanocomposites Based on an Organophilic Clay and Poly(styrene-*b*-butadiene) Copolymers," *J. Mater. Res.*, **12** [11] Nov., 3134-39 (1997).
9. Z. Wang and T. J. Pinnavaia, "Hybrid Organic-Inorganic Nanocomposites: Exfoliation of Magadiite Nanolayers in an Elastomeric Epoxy Polymer," *Chem. Mater.*, **10** 1820-26

- (1998).
10. J. W. Gilman, "Flammability and Thermal Stability Studies of Polymer Layered-Silicate (Clay) Nanocomposites," *Appl. Clay Sci.*, **15** 31-49 (1999).
 11. X. Kornmann, H. Lindberg, and L. A. Berglund, "Synthesis of Epoxy-Clay Nanocomposites; Influence of the Nature of the Clay on Structure," *Polymer*, **42** 1303-10 (2001).
 12. J.-X. Li, J. Wu, and C.-M. Chan, "Thermoplastic Nanocomposites," *Polymer*, **41** 6935-37 (2000).
 13. X. Fu and S. Qutubuddin, "Synthesis of Polystyrene-Clay Nanocomposites," *Mater. Latt.*, **42** 12-5 (2000).
 14. M. Vert, S. M. Li, G. Spenlehauer, and P. Guerin, "1. Biore-sorbability and Biocompatibility of Aliphatic Polyesters," *J. of Mater. Science-Materials in Medicine*, **3** [6] 432-46 (1992).
 15. R. Langer, "New Methods of Drug Delivery," *Science*, **249** 1527-33 (1990).
 16. S. Lannace, N. de Luca, and L. Nicolais, "Physical Characterization Incompatible Blends of Polymethylmethacrylate and Polycaprolactone," *J. Appl. Polym. Sci.*, **41** 2691-704 (1990).
 17. R. de Juana and M. Cortazar, "Study of the Melting and Crystallization Behavior of Binary Poly(ϵ -Caprolactone)/Poly(hydroxy ether of Bisphenol A) Blends," *Macromolecules*, **26** 1170-76 (1993).
 18. G. Detieuw, G. Groeninckx, and H. Reynaers, "Miscibility and Morphology of Binary Polymer Blends of Polycaprolactone with Solution-Chlorinated Polyethylenes," *Polymer*, **30** [4] 595-603 (1989).
 19. G. Detieuw, G. Groeninckx, and H. Reynaers, "Miscibility, Crystallization and Melting Behaviour, and Morphology of Binary Blends of Polycaprolactone with Styrene-Co-Maleic Anhydride Copolymers," *Polymer*, **30** [12] 2158-63 (1989).
 20. J. Heuschen, R. Jerome, and P. Teyssie, "Polycaprolactone-based Block Copolymers II: Morphology and Crystallization of Copolymers of Styrene or Butadiene and ϵ -Caprolactone," *J. Polym. Phys.*, **27** 523-44 (1989).
 21. P. B. Messersmith and E. P. Giannelis, "Synthesis and Barrier Properties of Poly(ϵ -Caprolactone)-Layered Silicate Nanocomposites," *J. of Polymer Sci.: Part A: Polymer Chem.*, **33** 1047-57 (1995).
 22. T. K. Chen, Y. I. Tien, and K. H. Wei, "Synthesis and Characterization of Novel Segmented Polyurethane/Clay Nanocomposite via Poly(ϵ -Caprolactone)/Clay," *J. of Polymer Sci.: Part A: Polymer Chem.*, **37** 2225-33 (1999).
 23. X. Kornmann, H. Lindberg, and L. A. Berglund, "Synthesis of Epoxy-Clay Nanocomposites: Influence of the Nature of the Clay on Structure," *Polymer*, **42** 1303-10 (2001).
 24. J.-O. Kim, T.-N. Kim, and S.-J. Cho, "A Study on the Synthesis of Organophilic Intercalations-Complex of [RCOOH]-Montmorillonite and on Its Swelling Behaviour," *J. Kor. Ceram. Soc.*, **31** [3] 282-90 (1994).
 25. P. B. Messersmith and E. P. Giannelis, "Synthesis and Barrier Properties of Poly(ϵ -Caprolactone) Layered Silicate Nanocomposites," *Chem. Mater.*, **10** 1047-57 (1994).
 26. T. K. Chen, Y. I. Tien, and K. H. Wei, "Synthesis and Characterization of Novel Segmented Polyurethane/Clay Nanocomposite via Poly(ϵ -Caprolactone)/Clay," *J. of Polymer Sci.: Part A: Polymer Chem.*, **37** 2225-33 (1999).