

# Formation of the Polycaprolactam between Layers of the [DEACOOH]-Montmorillonite Intercalations Complex and Its Characterization

Sung-Jun Cho<sup>†</sup>

Division for New Materials Engineering, Paichai University, Daejeon 302-735, Korea  
(Received February 13, 2006; Accepted March 6, 2006)

## ABSTRACT

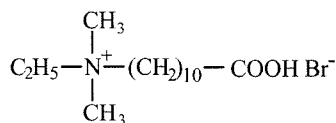
$\epsilon$ -caprolactam was polymerized in the layers of the [DEACOOH]-Montmorillonite intercalations complex at high temperatures ranging from 250°C to 260°C formed from Na-Montmorillonite and 10-Carboxy-n-decyldimethylethylammonium bromide to achieve [DEACOOH]-Polycaprolactam-Montmorillonite, in which an inorganic polymer (montmorillonite) is chemically combined with an organic polymer (polycaprolactam). The results of X-ray and IR analyses for the samples obtained after polymerization showed that the polymerization reaction was successfully accomplished. For the purpose of studying the polymeric reaction product more precisely, the polymerized product was separated from the silicate layers and analyzed with an X-ray diffractometer and an IR-spectrometer. A comparison of the results of the X-ray and IR analyses of the separated polymer and the polymer that was synthesized by the reaction of  $\epsilon$ -caprolactam solely with the organic cation without montmorillonite showed that the obtained both polymers are identical compounds.

**Key words:**  $\epsilon$ -caprolactam, [DEACOOH]-Montmorillonite intercalations complex, Inorganic polymer, Organic polymer, 10-Carboxy-n-decyldimethylethylammonium bromide

## 1. Introduction

Composite materials are widely useful in various fields such as aeronautics, communications and the automotive industries. It is well known that clays have a good potential for use as filler materials in polymer matrix composites, as they have a high aspect ratio and a platy morphology.<sup>1,2)</sup> To improve the chemical, physical, mechanical, electrical and thermal properties (e.g. chemical resistance, strength, toughness, stiffness, elasticity, isolation) of pure polymer materials without reinforcement or the use of a filler, investigations concerning the synthesis of clay-polymer nanocomposites through a reinforcement with a clay of pure polymer materials has been very active.<sup>3-6)</sup> Theoretically, it is possible to form inorganic-organic complexes in which both- an inorganic polymer (i.e. inorganic montmorillonite) and an organic polymer- are chemically combined, studies in this research area have also been active.<sup>7-18)</sup>

Thus, in this research the creation of such a plastic composite reinforced with montmorillonite was investigated. For this purpose a metal ion, the sodium ion (Na<sup>+</sup>) was substituted with the organic cation with a long alkyl chain that follows to ensure that there is enough reaction space for the chemical reaction between the montmorillonite layers initially;



10-Carboxy-n-decyldimethylethylammonium bromide  
(will be abbreviated as [DEACOOH] Br after now)

After the organic monomer ( $\epsilon$ -caprolactam) was intercalated into the layers of this [DEACOOH]-Montmorillonite intercalations complexes the monomer between the interlamellar spaces was polymerized by a polycondensation reaction at high temperatures that ranged from 250°C to 260°C, and formed inorganic-organic complexes in which montmorillonite as an inorganic polymer is chemically linked with polycaprolactam as an organic polymer.

## 2. Experimental Procedure

### 2.1. Materials

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

### 2.2. Method

#### 2.1.1. Formation of [DEACOOH]-Montmorillonite

A water solution of [DEACOOH] Br was added to a sus-

<sup>†</sup>Corresponding author : Sung-Jun Cho  
E-mail : sjcho@pcu.ac.kr  
Tel : +82-42-520-5394 Fax : +82-42-520-5394

pension from Na-Montmorillonite and distilled water while stirring. The entire mixture was then left at 65°C for 48 h under occasional stirring, and thereafter centrifuged as to isolated the swelling solution from the product, a [DEACOOH]-Mont intercalations complex. The [DEACOOH]-Mont was initially dried at 100°C in an oven and continuously at 65°C in vacuum of  $10^{-3}$  torr for 24 h.

### 2.2.2. Formation of [DEACOOH]- $\epsilon$ -Caprolactam-Montmorillonite

14 g of [DEACOOH]-Mont and 9.9 g of  $\epsilon$ -caprolactam were well mixed with mortar. This mixture was put into a 100 mL round flask and then left under a  $N_2$ -atmosphere for 30 min under occasional stirring. Thereafter, the round flask containing the mixture was heated at 75°C for 30 min, cooled slowly to 37°C, and mixed well with mortar. Following this the sample was put into the reaction flask again, left under a  $N_2$ -atmosphere for 30 min with occasional stirring, heated at 75°C for 30 min, cooled slowly to 37°C and left at this temperature for 2 days. This procedure was repeated an additional two times.

### 2.2.3. Polycondensation of $\epsilon$ -Caprolactam in the Interlamellar Spaces

A thick horosilicate ampule was preheated with a heat gun to remove moisture from it, then the [DEACOOH]- $\epsilon$ -caprolactam-Montmorillonite, synthesized by the method described in Chapter 2.2.2 was put into the preheated ampule and the sample was evacuated, sealed and heated at a temperature range of 250°C to 260°C for 48 h to polymerize the  $\epsilon$ -caprolactam into the interlamellar spaces of the [DEACOOH]-Montmorillonite intercalations complex.

### 2.2.4. Polycondensation of $\epsilon$ -Caprolactam and [DEACOOH] Br without Montmorillonite

In order to compare the polymer obtained from the above procedure with the organic monomer,  $\epsilon$ -caprolactam, alone was polymerized with the organic cation, [DEACOOH] Br without montmorillonite at 250°C for 48 h. The product was purified by washing with water and drying at 65°C for 24 h in a high vacuum of  $10^{-3}$  torr.

### 2.2.5. Isolation of Polycaprolactam from [DEACOOH]-Mont

The polycaprolactam polymerized in the layers of [DEACOOH]-Mont was isolated by the decomposition of silicate lattice using an ammonium hydrogen fluoride ( $NH_4[HF_2]$ ) solution.

Polycaprolactam-Montmorillonite was mixed with an excess amount of 1 n  $NH_4[HF_2]$ -solution. The mixture solution was then left at room temperature for 2 days under stirring, and thereafter conc.  $NH_4OH$  solution was added to the solution, which had a pH 3.5 at the beginning such that it was a neutral or weak alkalic. The precipitate was isolated from the solution by filtration, dried at 65°C for a short time initially in an oven and then continuously in a high

vacuum of  $10^{-3}$  torr for 24 h. The dried sample was mixed with an excess amount of 100% glacial acetic acid, and the mixture was filtered at 60~70°C. The separated solution phase for glacial acetic acid was then treated with an excess amount of diethyl ether. The polymer precipitate was separated and dried at 65°C for 24 h in a high vacuum ( $10^{-3}$  torr).

## 3. Characterization

Infrared spectroscopic measurements on the Na-Montmorillonite, [DEACOOH]-Mont, [DEACOOH]-polycaprolactam-Montmorillonite, the polymer material separated from the inorganic/organic hybrid and the pure polymer synthesized without montmorillonite were performed using a Prekin Elmer 325 spectrometer.

The [DEACOOH]-Mont intercalations complex, [DEACOOH]- $\epsilon$ -caprolactam-Montmorillonite and [DEACOOH]-polycaprolactam-Montmorillonite were characterized by X-ray diffractometry (Philips Novello) using  $Cu K_{\alpha}$ -radiation ( $\lambda=1.5418 \text{ \AA}$ ) with a scan speed of 1.00 deg/min.

The reaction products obtained after the polycondensation of caprolactam in the layers of the [DEACOOH]-Montmorillonite intercalation complex between 250°C and 260°C were also analyzed with a transmission electronic microscope (TEM; JEOL 100 LX with 100 kV Accelerating Voltage).

## 4. Results and Discussion

### 4.1. Results of Intercalations Complexes

The organophilic [DEACOOH]-Montmorillonite intercalations complex obtained from the reaction of Na-Montmorillonite with [DEACOOH] Br was characterized with an X-ray diffractometer under the following conditions:

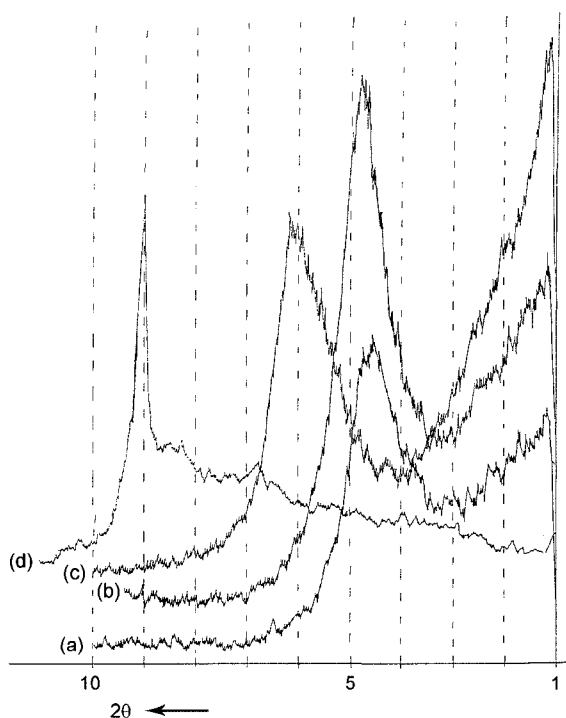
- The equilibrium solution after the exchange reaction was centrifuged; the solid residue was analyzed with X-ray diffractometry in a still wet condition from the adherent equilibrium solution (Fig. 1(a)).
- Thereafter the centrifuged solid sample was washed eight times with distilled water until it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

The results measured with X-ray diffractometry are shown in Table 1 and Fig. 1 which together show that the basal spacing values between the reaction products, [DEACOOH]-Mont and the starting material, Na-montmorillonite, are fairly different. The Na-Montmorillonite used as a starting material swells toward infinitely under distilled water, i.e. the layers of the crystals separate into individual layers. For this reason, the attractive interactions between adjacent layers will reduce. After drying under a high vacuum its basal spacing falls to 9.8~10.1  $\text{\AA}$  (Fig. 1(d)).

In the case of [DEACOOH]-Mont, a basal spacing of

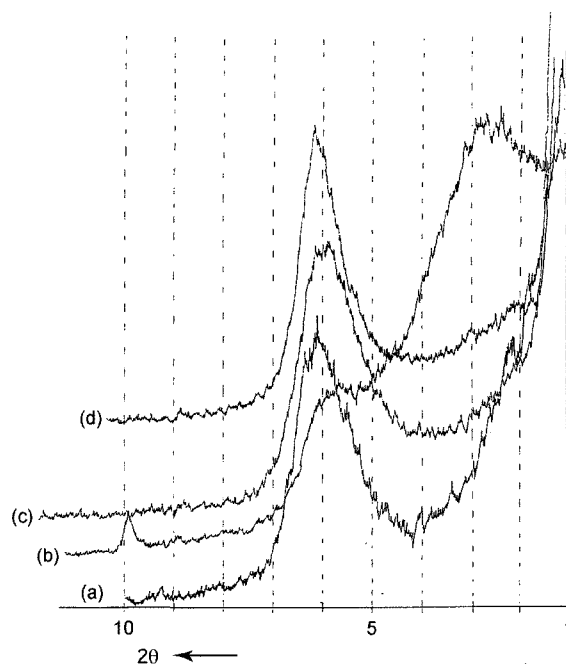
**Table 1.** Basal Spacings(Å) Measured after the Cation Exchange Reaction

Sample treatment	Basal spacing(Å) of	
	Reaction product	Na-Montmorillonite
After more than 48 h exchange time, under exchange solution	19.57	-
After eight times washing, measured under water	18.49	Toward infinity
After 24 h drying in a high vacuum at 65°C	14.48	9.8~10.1

**Fig. 1.** XRD patterns of [DEACOOH]-Mont; (a) after 48 h exchange-time, under exchange solution, (b) after washing eight times under water, (c) after 24 h drying in a high vacuum at 65°C, and (d) Na-Montmorillonite dried in a high vacuum at 65°C for 24 h.

19.57 Å is obtained in the exchange solution, but it lies at 18.49 Å with a reduction of 1.08 Å after washing eight times with water so as to make it free from halide. In this condition, it was obvious that in the sample large quantity of water remains between the layers of the intercalations complex. For this reason, the sample was dried at 65°C in a high vacuum ( $10^{-3}$  torr) for 24 h, and following this a closed packing was obtained and the basal spacing also decreased to 14.48 Å with a reduction of 4.01 Å. This is a feasible value, as the density of the charge of montmorillonite used in this study was specially small.

Fig. 2 shows the XRD-patterns for the [DEACOOH]-ε-caprolactam-Montmorillonite synthesized by the reaction of [DEACOOH]-Mont with ε-caprolactam. As shown in Table 2 and Fig. 2 the X-ray pattern of the [DEACOOH]-ε-caprolactam-Montmorillonite is quite different from that of the starting material, [DEACOOH]-Mont. This suggests that the caprolactam is successfully intercalated into the layer of [DEACOOH]-Mont. But from Fig. 2 it is seen that the X-ray

**Fig. 2.** XRD patterns of [DEACOOH]-Mont with ε-caprolactam; (a) [DEACOOH]-Mont as a starting material, (b) after intercalation of ε-caprolactam into [DEACOOH]-Mont, (c) after drying of (b) in a high vacuum directly after the exchange reaction, and (d) after extraction with methanol and following drying in the high vacuum of (b).

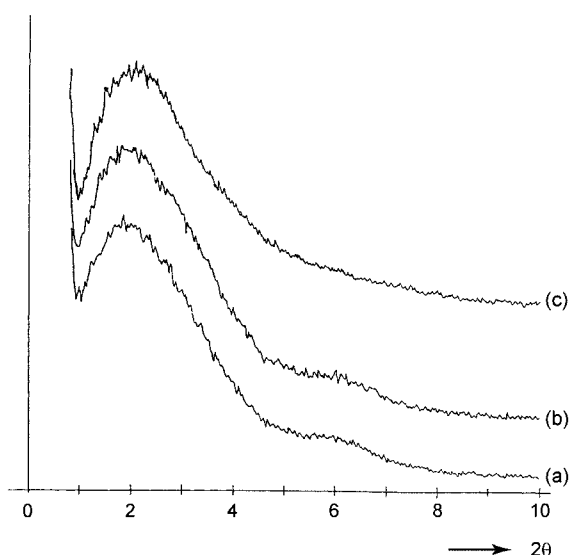
patterns obtained following the process of drying in the high vacuum directly after the exchange reaction, and extracting with methanol following the drying in high vacuum are nearly identical to that of the starting material, [DEACOOH]-Mont. This suggests that the intercalated ε-caprolactam between the layers of [DEACOOH]-Mont were extensively removed again from the layers.

#### 4.2. Results of Polycondensation

In order to determine if the polycondensation of ε-caprolactam in the layers of [DEACOOH]-Montmorillonite intercalations complex were successful the polymerized sample was treated in a high vacuum ( $10^{-3}$  torr) at 65°C for 24 h. Under these conditions the unreacted ε-caprolactam intercalated only in the silicate layers, was removed from the layers again, and the basal spacing fell to ca. 14.5 Å which was the value of the starting material, [DEACOOH]-Mont dried in the high vacuum. Independent of this procedure, extraction analyses of samples were performed with the sol-

**Table 2.** Results of the Polymerization of  $\epsilon$ -Caprolactam in [DEACOOH]-Montmorillonite

Sample treatment	Basal spacings( $\text{\AA}$ ) after reaction of [DEACOOH]-Mont. with monomer before polymerization	Basal spacings( $\text{\AA}$ ) for 48 h at	
		250°C	260°C
Starting material for polymerization	36.38		
After polymerization		45.89	58.85
Dried in a high vacuum at 65°C, 24 h	15.26	43.31	55.35
After extraction with methanol and dried in a high vacuum at 65°C, 24 h	14.49	42.83	54.67

**Fig. 3.** XRD patterns of [DEACOOH]-Mont with  $\epsilon$ -caprolactam after polymerization; (a) after polymerization for 36 h at 250°C, (b) after drying in a high vacuum at 65°C 24 h, and (c) after extraction with methanol and following drying in high vacuum of (a).

vents where only a monomer or small oligomers were soluble, but not the polymer. The results measured with the X-ray diffractometer are shown in Table 2 and Fig. 3.

From the results of Table 2 and the X-ray diffraction patterns in Fig. 2 it is shown that the  $\epsilon$ -caprolactam was nearly fully removed from the layers of [DEACOOH]-Mont, if the caprolactam was not polymerized in the layers, and was dried at 65°C for 24 h in a high vacuum directly after the intercalation reaction (Fig. 2(c)) and after extraction with solvent (here methanol) (Fig. 2(d)). However, the results of Table 2 and Fig. 3 show that the  $\epsilon$ -caprolactam was not removed from the layers after the polymerization. This suggests that a polymerization of  $\epsilon$ -caprolactam was successfully performed between the layers of [DEACOOH]-Mont.

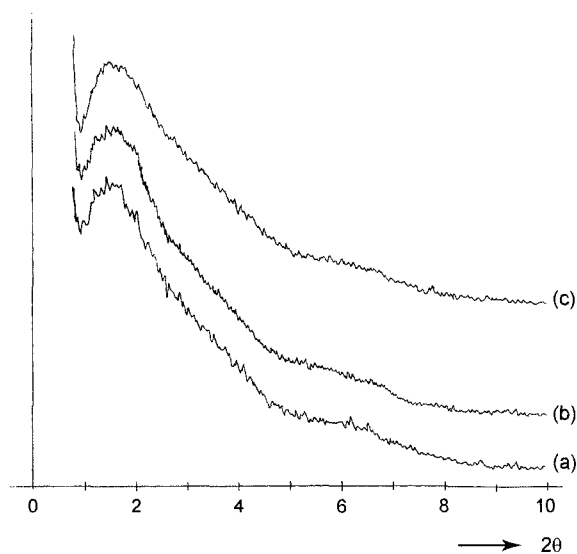
In the second column of the Table 2 the basal spacings of the reaction products, [DEACOOH]-Caprolactam-Montmorillonites, which were synthesized by the intercalations reaction of  $\epsilon$ -caprolactam into [DEACOOH]-Mont and will be used as a starting material for the polymerization of the organic monomer are summarized. The basal spacing of [DEACOOH]-Caprolactam-Montmorillonite before polymer-

ization was 36.38  $\text{\AA}$ , but this was reduced to 15.26  $\text{\AA}$  after the intercalations reaction and the drying at 65°C, for 24 h in a high vacuum. This reduction is caused by the removal of almost all of the  $\epsilon$ -caprolactam from the layers in the high vacuum by vaporization. Table 2 and Fig. 2 show also that in case of the extraction with the solvent, methanol, in which the monomer was soluble and the following the drying in the high vacuum at 65°C for 24 h the monomer,  $\epsilon$ -caprolactam, was also removed from the layers and the basal spacings fell to 14.49  $\text{\AA}$ .

In the next two columns of the Table 2 the basal spacings of the products obtained after polycondensation between 250°C and 260°C for 48 h are summarized. From the results of the Table 2 it is shown that in every case the basal spacing increased with the reaction temperature. After polymerization at 250°C the basal spacing was 45.89  $\text{\AA}$ , while the basal spacing obtained after polycondensation at 260°C was 58.85  $\text{\AA}$ . From these results it is clear that the polymerization successfully proceeded, and that the higher basal spacing was obtained with a higher reaction temperature.

It is possible to observe more precisely the polymerization state by checking the basal spacings measured directly after drying at 65°C for 24 h in a high vacuum. While the basal spacings obtained before polymerization lies at 14.48  $\text{\AA}$ , the basal spacings of the sample synthesized after polymerization between 250°C and 260°C were 45.89  $\text{\AA}$  and 58.85  $\text{\AA}$ , respectively, which decreased to 43.31  $\text{\AA}$  and 55.35  $\text{\AA}$ , respectively, after drying at 65°C for 24 h in a high vacuum, and then to 42.83  $\text{\AA}$  and 54.67  $\text{\AA}$ , respectively, after the extraction with methanol and the continued drying at 65°C for 24 h in a high vacuum. Therefore a large difference (greater than 28  $\text{\AA}$ ) exists between the basal spacings of the two cases (before and after polymerization), from which it can be deduced that large amounts of the monomer ( $\epsilon$ -caprolactam) were removed from the layers, if the monomer is only intercalated between the interlamellar spaces without being polymerized. In general, it is shown from the results of Table 2 that the higher the reaction temperature is, the greater the basal spacing obtained.

Comparing Figs. 2 and 3 it is apparent that the X-ray peaks obtained after polymerization are not sharp and are far broader than those measured before the polymerization. For this reason the basal spacings of the X-ray patterns after polymerization are much less precise than those obtained before the polymerization. Therefore due to the dif-



**Fig. 4.** XRD patterns of [DEACOOH]-Mont with  $\epsilon$ -caprolactam after polymerization; (a) after polymerization for 36 h at 260°C, (b) after drying in high vacuum at 65°C 24 h, and (c) after extraction with methanol and following drying in the high vacuum of (a).

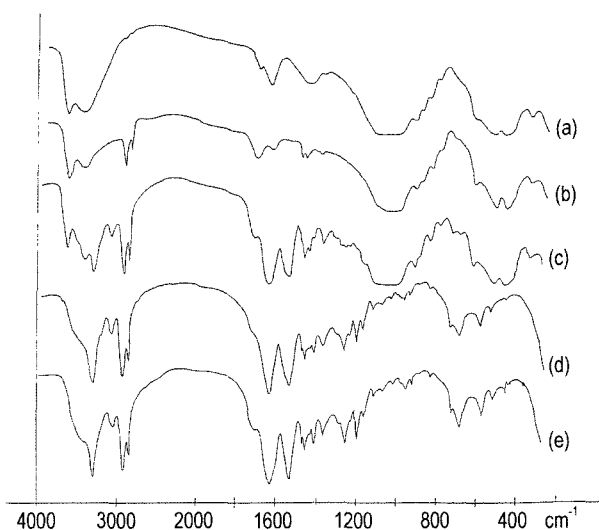
difficulty in measuring the exact basal spacings from the X-ray peaks after polymerization, it has to be considered that only rough basal spacings could be taken in Table 2 and that the limit of error is 3 Å or more.

#### 4.3. Results of IR-Analyses

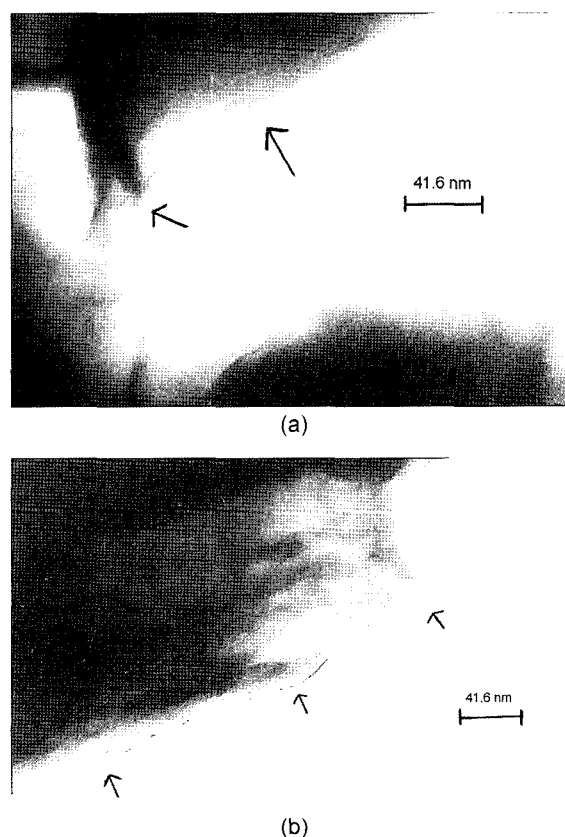
The results of IR-analyses for each sample are shown in Fig. 4(a)–(e). The IR-spectrum for Na-Montmorillonite is shown in Fig. 4(a). This spectrum includes somewhat characteristic broad peaks. Fig. 4(b) shows the IR-spectrum for [DEACOOH]-Mont with the cation in the interlamellar space. In this spectrum it is shown that the sharp peaks in the region from 2828 to 2915  $\text{cm}^{-1}$  and from 1468–1490  $\text{cm}^{-1}$  which did not exist in the spectrum for Na-Montmorillonite and are derived from the organic cation intercalated between the layers.

Fig. 4(c) shows the IR-spectrum for [DEACOOH]-Polycaprolactam-Montmorillonite sample synthesized by the polymerization of  $\epsilon$ -caprolactam in the interlamellar space of the [TEACOOH]-Mont intercalations complex, extracted with methanol solvent to remove the caprolactam which was not polymerized, and then dried at 65°C for 24 h in high vacuum. In this case it is possible to observe the additional sharp peaks.

In Fig. 4(d) the IR-spectrum for the sample separated from the interlayer spaces of montmorillonite after the decomposition of [DEACOOH]-Polycaprolactam-Montmorillonite with  $\text{NH}_4[\text{HF}_2]$  was demonstrated, in order to compare it to the spectrum for the polymer synthesized by the reaction of  $\epsilon$ -caprolactam with [DEACOOH]-Mont without montmorillonite. The comparison is shown in Fig. 4(e). Comparing Fig. 4(d) with Fig. 5(e) it was observed that both



**Fig. 5.** IR-spectrums for (a) Na-Montmorillonite, (b) [DEACOOH]-Montmorillonite, (c) [DEACOOH]-Polycaprolactam-Montmorillonite, polymerized for 36 h at 250°C, extracted with methanol and dried in high vacuum at 65°C for 24 h, (d) polymer, isolated from the interlayer space of montmorillonite (original polymerization in interlayer space at 250°C for 36 h, extracted with methanol, then isolated by a  $\text{NH}_4[\text{HF}_2]$ -process, and (e) polycaprolactam, synthesized without montmorillonite, after extraction with water and dried in high vacuum at 65°C for 24 h.



**Fig. 6.** TEM pictures of the montmorillonite/polycaprolactam nanocomposites at (a) 250°C and (b) 260°C.

polymers, synthesized under different reaction conditions, are identical compounds.

It is clear from the polymerization experiments and the results of the IR-Spectrums (Fig. 4(c), (d), and (e)) that a chemical reaction (polymerization) in the interlamellar space of [DEACOOH]-Mont occurred.

#### 4.4. Results of TEM-Analyses

From analyses by a transmission electronic microscope of the reaction products obtained after the polycondensation of caprolactam between the layers of the [DEACOOH]-Montmorillonite intercalation complex (Fig. 6), the appearance of the clay mineral as a reinforcement in the polymerized products can be seen. Fig. 6 shows the repeating arrangement of the layers of montmorillonite mineral used as reinforcement in the polymer matrix of the montmorillonite/polycaprolactam composites.

### 5. Conclusions

In this research, an attempt was made to polymerize  $\epsilon$ -caprolactam in the interlamellar space of a [DEACOOH]-Montmorillonite intercalations complex at the high temperatures of 250°C to 260°C to achieve [DEACOOH]-Polycaprolactam-Montmorillonite in which the montmorillonite (inorganic polymer) is chemically bonded to the organic polymer (polycaprolactam). The following results were founded:

1. The basal spacings for the samples obtained after polymerization lie at 48.83 Å to 54.67 Å in a dried condition in a high vacuum, while those for the samples before polymerization lie at 14.49 Å in the same condition.

2. Especially it was observed that the higher the reaction temperature, the higher the obtained basal spacing.

3. From a comparison between the IR-spectrum of the starting material before polymerization and that of the product obtained after polymerization, it was observed that the polymerization appeared in the interlamellar space of the intercalations complex.

4. Comparing the IR-spectrum for the sample isolated from the layers of [DEACOOH]-Mont after the polymerization of  $\epsilon$ -caprolactam in the interlamellar space of [DEACOOH]-Mont with that for the polymer synthesized by the reaction of  $\epsilon$ -caprolactam with only the organic cation, [DEACOOH] Br, without montmorillonite it was made clear that the both polymers synthesized under the different reaction conditions were identical compounds.

5. Repeating arrangement of the layers of the reinforced montmorillonite in the polymer matrix of the montmorillonite/polycaprolactam composites were also observed by TEM.

From the results as a whole, it appears that the polymerization was successfully accomplished in the interlamellar space of the [DEACOOH]-Mont intercalations complex.

### REFERENCES

1. B. K. G. Theng, "Formation and Properties of Clay-Polymer Complexes," Elsevier, New York (1979).
2. E. P. Giannelis, "JOM," **44** 28 (1992).
3. D.-I. Hans Domininghaus, "Fillers for Plastics(Zusatzstoffe für Kunststoffe)," *Zehner & Huethig Verlag GmbH Speyer am Rhein*, 114-20 (1978).
4. A. J. Dankwerth, "Kaolin Clay," *Modern Plastics Encyclopedia*, 393-94 (1972/73).
5. J. H. Etlinger, "Glass," *Modern Plastics Encyclopedia*, 393 (1972/73).
6. R. B. Seymour, "Fillers for Polymers," *Modern Plastics Encyclopedia*, 382-88 (1972/73).
7. T. Lan and T. J. Pinnavaia, "Clay-Reinforced Epoxy Nanocomposites," *Chem. Mater.*, **6** 2216-19 (1994).
8. H. Shi, T. Lan, and T. J. Pinnavaia, "Interfacial Effects on the Reinforcement Properties of Polymer-Organoclay Nanocomposites," *Chem. Mater.*, **8** 1584-87 (1996).
9. R. A. Vala, K. D. Jandt, E. J. Kramer, and E. P. Giannelis, "Microstructural Evolution of Melt Intecalated Polymer-Organically Modified Layered Silicates Nanocomposites," *Chem. Mater.*, **8** 2628-35 (1996).
10. 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] 3134-39 (1997).
11. S.-J. Cho, "A Study on the Polymerization of  $\epsilon$ -Caprolactam in [RCOOH]-Montmorillonite Intercalations Complex(in Korean)," *J. Kor. Ceram. Soc.*, **36** [2] 1-8 (1999).
12. S.-J. Cho, "Synthesis and Characterization of Polycaprolactone Nanocomposites Reinforced with Montmorillonite(in Korean)," *J. Kor. Ceram. Soc.*, **41** [6] 425-29 (2004).
13. S.-J. Cho, "Polycondensation of  $\epsilon$ -Caprolactone in the Layer Spaces of Organophilic Montmorillonite and Its Characterization(in Korean)," *J. Kor. Ceram. Soc.*, **42** [4] 224-31 (2005).
14. 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).
15. J. W. Gilman, "Flammability and Thermal Stability Studies of Polymer Layered-Silicate (Clay) Nanocomposites," *Appl. Clay Sci.*, **15** 31-49 (1999).
16. X. Kornmann, H. Lindberg, and L. A. Berglund, "Synthesis of Epoxy-Clay Nanocomposites," *ANTEC '99*, 1623-27.
17. J.-X. Li, J. Wu, and C.-M. Chan, "Thermoplastic Nanocomposites," *Polymer*, **41** 6935-37 (2000).
18. X. Fu and S. Qutubuddin, "Synthesis of Polystyrene-Clay Nanocomposites," *Mater. Lett.*, **42** 12-5 (2000).