

# Formation and Characterization of Chemically Combined [TEACOOH]-Montmorillonite/Polycaprolactone Nanocomposites

Sung-Jun Cho<sup>†</sup>

Department of Nanopolymer Materials Engineering, Pai Chai University, Daejeon 302-735, Korea  
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## ABSTRACT

A [TEACOOH]-Montmorillonite intercalations complex obtained from Na-Montmorillonite and 10-Carboxy-n-triethylammonium bromide was used to attempt the polymerization of  $\epsilon$ -caprolactone between the layer spaces of the intercalations complex to achieve Montmorillonite-Polycaprolactone nanocomposites in which the inorganic material (montmorillonite) is chemically combined with the organic polymer (polycaprolactone). The results of X-ray-, IR-, and TEM-analyses for samples obtained after polymerization showed that a polycondensation reaction was successfully produced. For a more precise investigation of the polymeric reaction products the polymerized products were separated from the silicate layers and analyzed with an IR-spectrometer. A comparison of the results of the IR-analyses of the separated polymer with that of the polymer synthesized by the reaction of  $\epsilon$ -caprolactone with only the organic cation and without montmorillonite showed that the two obtained polymers are the same compound.

**Key words:**  $\epsilon$ -caprolactone, Nanocomposites, Inorganic material, Organic polymer

## 1. Introduction

Montmorillonite which belongs to the smectite group<sup>1,2)</sup> is a layered mica-type silicate<sup>3,4)</sup> used very widely in the formation of intercalations complexes as well as in industry due to its ability of increase its volume through one-dimensional innercrystalline swelling.<sup>5,6)</sup> In particular, there exists an exchangeable metal cation in the interlayer space of montmorillonite. Therefore, if this metal ion is replaced with an organic cation with at least one long chain by a cation exchange reaction, organophilic montmorillonite intercalations complexes with different material properties can be formed. This type of organophilic montmorillonite can be used not only as a filler for lacquer, grease, cosmetics, or paint,<sup>3)</sup> but also in refining factory waste water contaminated by organic compounds.<sup>7,8)</sup> It can also be used as a model system in which its behavior under various conditions could be investigated.<sup>9-11)</sup>

Clay has a very small particle size, exists abundantly in nature and is a very useful material in the economic and environmental aspects. It has excellent mechanical and chemical properties; thus, it is broadly used as a reinforcement material for polymers. To improve the chemical, physical, mechanical, electrical and thermal properties such as the chemical resistance, strength, toughness, stiffness, elasticity, or isolation of pure polymer materials without a reinforcement material or fillers, study on the synthesis of clay-

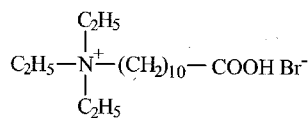
polymer nanocomposites by via a reinforcement of pure polymer materials with clay minerals as a reinforcement material has been very active.<sup>12-15)</sup> Theoretically, it is possible to form inorganic-organic complexes in which both inorganic material (for example inorganic montmorillonite) and organic material are chemically combined; studies in this research area are also very active.<sup>16-24)</sup>

Poly( $\epsilon$ -caprolactone)(PCL) is a type of biodegradable aliphatic polymer that has seen much recent interest for use in pharmaceutical controlled-release systems, medical devices and in degradable packaging.<sup>25-27)</sup> In particular, PCL has excellent commercial use as a copolymer with polyvinylchloride, and acrylonitrile-butadiene-styrene.<sup>28-31)</sup> However, the future development of additional potential uses of PCL is greatly limited, as it has a low melting point and low glass transition temperature ( $T_g$ ). Therefore, it can only be applied in various fields, if its mechanical properties can be improved by reinforcing it with reinforcement materials or fillers such as clay.

Clay can alter its properties if the metal cations in its interlayer spaces are substituted with other cations, especially with organic cations. This implies that the properties of clay can be completely changed by the type of the organic cation intercalated between the layers of clay. For example, Giannelis<sup>32)</sup> and Wei<sup>33)</sup> 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.<sup>34)</sup> In the present study, quaternary ammonium salt (10-carboxy-n-decyltriethylammonium bromide)

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

is used as an organic cation with a long alkyl chain synthesized by a method described in an earlier publication.<sup>35)</sup>



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

In other research, organically modified montmorillonite (OMM) was synthesized by a cation exchange reaction between Na-montmorillonite and primary ammonium salt, which was prepared in situ from aminolauric acid and concentrated HCl in distilled water.<sup>36,37)</sup> Subsequently, the poly( $\epsilon$ -caprolactone)-montmorillonite nanocomposite (PCLM) was synthesized from OMM and  $\epsilon$ -caprolactone in a vial at 170°C (oil bath temperature). However, in this research, a quaternary ammonium salt as an organic cation was initially prepared, and the OMM was subsequently formed by a cation exchange reaction between Na-montmorillonite and the quaternary ammonium salt. The OMM was then treated with  $\epsilon$ -caprolactone to obtain organic cation- $\epsilon$ -caprolactone-montmorillonite intercalations complex (OCM), and the OCM was heated at various temperatures higher than 170°C, i.e., 220°C, 230°C, and 240°C in a sealed evacuated ampoule for the polymerization reaction to obtain PCLM.

## 2. Experimental Procedure

### 2.1. Materials

$\epsilon$ -caprolactone used as a starting material for the organic polymer and n-undecanoic acid bromide, and triethylamine used in preparing the organic cation 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 [TEACOOH]-Montmorillonite intercalations complex, [TEACOOH]- $\epsilon$ -caprolactone-Montmorillonite, [TEACOOH]-polycaprolactone-Montmorillonite and the separated samples treated with a  $\text{NH}_4[\text{HF}_2]$ -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 of the pure Na-Montmorillonite, the organophilic [TEACOOH]-Montmorillonite intercalations complex, [TEACOOH]-polycaprolactam-Montmorillonite, the polymer material separated from this inorganic/organic hybrid and the pure polymer synthesized without montmorillonite were also performed using a 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. Preparation of the Organophilic [TEACOOH]-Montmorillonite Intercalations Complex

A suspension from Na-Montmorillonite and distilled water was prepared and a water solution of [TEACOOH] Br was added to the suspension while stirring. The intact mixture was then left at 65°C for 48 h under occasional stirring and thereafter centrifuged so that the swelling solution could be separated from the product, the organophilic [TEACOOH]-Montmorillonite intercalations complex. This [TEACOOH]-Montmorillonite was washed with distilled water and then dried at 100°C initially in an oven, and continuously at 65°C in a vacuum of  $10^{-3}$  torr for 24 h.

### 2.4. Preparation of [TEACOOH]- $\epsilon$ -Caprolactone-Montmorillonite

Stoichiometrical amounts of the organophilic [TEACOOH]-Montmorillonite and  $\epsilon$ -caprolactone were put into a 100 mL round flask and well mixed with mortar, and the mixture was then left in an  $\text{N}_2$ -atmosphere for 30 min under occasional stirring. The round flask with the mixture was then heated at 95°C (oil bath) for 30 min, cooled slowly up to 50°C, and well mixed with mortar. The sample was then put into the reaction flask again, left in the  $\text{N}_2$ -atmosphere for 30 min with occasional stirring, heated to 95°C for 30 min, cooled slowly up to 50°C and left at this temperature for 3 days. This procedure was repeated 3 additional times.

### 2.5. Polycondensation of $\epsilon$ -Caprolactone in the Layers of [TEACOOH]-Montmorillonite

[TEACOOH]- $\epsilon$ -caprolactone-Montmorillonite was put into a thick horosilicate ampoule that was preheated with heat gun to remove the moisture. The ampoule with the sample was then evacuated, sealed and heated to 220°C, 230°C, and 240°C for 48 h to polymerize the  $\epsilon$ -caprolactone between the layers of [TEACOOH]-Montmorillonite.

### 2.6. Polycondensation of $\epsilon$ -Caprolactone and [TEACOOH] Br without Montmorillonite

In order to compare with the polymer obtained from the above procedure, the organic monomer  $\epsilon$ -caprolactone alone was polymerized with the organic cation, [TEACOOH] 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 a high vacuum of  $10^{-3}$  torr.

### 2.7. Isolation of Polycaprolactone from the Layers of [TEACOOH]-Montmorillonite

The poly( $\epsilon$ -caprolactone) polymerized in the layer spaces of the organophilic [TEACOOH]-Montmorillonite intercalations complex was isolated by the decomposition of the silicate lattice using an ammonium hydrogen fluoride ( $\text{NH}_4[\text{HF}_2]$ ) solution. The pure Na-Montmorillonite, which was not polymerized, i.e., did not include any organic compound, was also decomposed in the same way for the purpose of comparison.

Na- and polycaprolactone-montmorillonite were mixed

with an 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 a conc. ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) solution was added to each. A pH of 3.5 resulted at the beginning, leaving it neutral or weak-alkalic. The precipitate was separated from the solution by the filtration, dried at  $65^\circ\text{C}$  for a short time in an oven initially and then continuously in a high vacuum of  $10^{-3}$  torr for 24 h. This dried sample was mixed with an excess amount of 100% glacial acetic acid, and the mixture was filtered at  $60\sim 70^\circ\text{C}$ . The separated glacial acetic acid phase was then treated with an excess of diethyl ether for precipitation. The polymer precipitate was then separated and dried at  $65^\circ\text{C}$  for 24 h in high vacuum ( $10^{-3}$  torr).

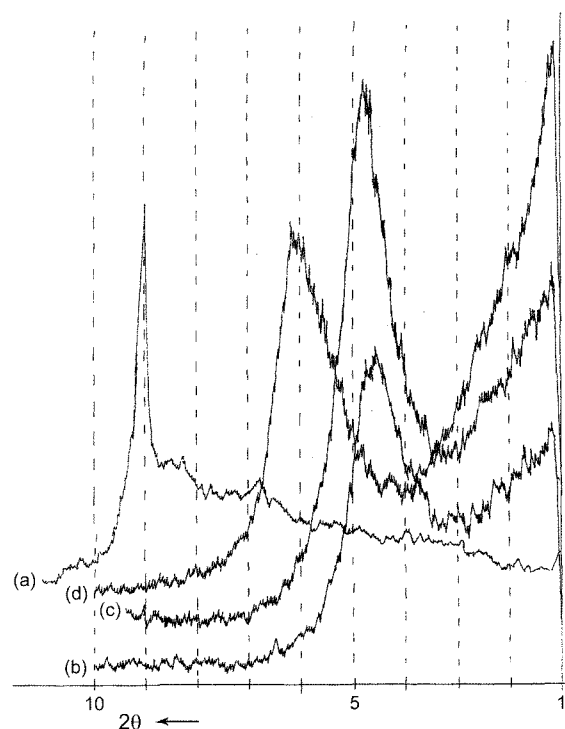
### 3. Results and Discussion

#### 3.1. Organophilic [TEACOOH]-Montmorillonite Intercalations Complex

The organophilic [TEACOOH]-Montmorillonite intercalations complex synthesized by the cation exchange reaction of Na-Montmorillonite with [TEACOOH] Br was characterized with an X-ray diffractometer under the following conditions:

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

The obtained results from the measurements with the X-ray diffractometer are summarized in Table 1, from which it was observed that the basal spacing values between the starting material, Na-montmorillonite, and the reaction products, [TEACOOH]-Mont, are quite different. The Na-Montmorillonite used as a starting material swells considerably under distilled water, i.e., the layers of the crystals separate to the individual layers. Thus, the attractive interactions between the adjacent layers will reduce. After drying under a high vacuum of  $10^{-3}$  torr at  $65^\circ\text{C}$  for 24 h, its basal spacing falls to  $9.8\sim 10.1$  Å. The X-ray diffraction (XRD) patterns for the summarized data in Table 1 are



**Fig. 1.** X-ray diffraction patterns of [TEACOOH]-Montmorillonite; (a) Na-Montmorillonite dried in a high vacuum at  $65^\circ\text{C}$  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 a high vacuum at  $65^\circ\text{C}$ .

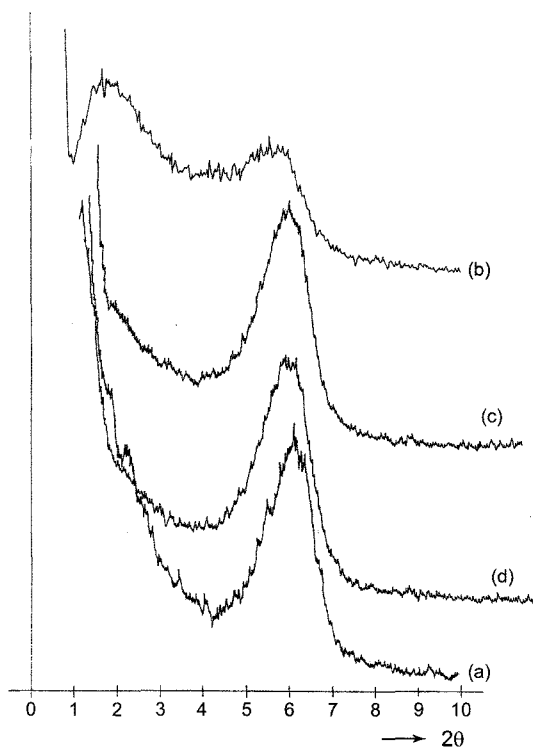
demonstrated in Fig. 1.

In case of the [TEACOOH]-Montmorillonite synthesized by the cation exchange reaction of Na-Montmorillonite with [TEACOOH] Br, a basal spacing of  $19.60$  Å was obtained under the exchange solution, which is, however,  $18.52$  Å with the reduction of  $1.08$  Å after washing eight times with water until it was free of halide. Under this condition, it is clear that the sample retains much water between the layers of the intercalations complex. Therefore, the sample was dried at  $65^\circ\text{C}$  in a high vacuum of  $10^{-3}$  torr for 24 h, leading to close packing. The basal spacing also decreased to  $14.52$  Å with a reduction of  $4.0$  Å.

Fig. 2 shows the XRD-patterns for the [TEACOOH]- $\epsilon$ -caprolactone-Montmorillonite obtained by the reaction between the organophilic [TEACOOH]-Montmorillonite intercalations complex and  $\epsilon$ -caprolactone. From Fig. 2 it is clear that the XRD pattern of the [TEACOOH]- $\epsilon$ -caprolactone-Montmorillonite is quite different from that of the

**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	19.60	-
After eight times washing, measured under water	18.52	toward infinity
After 24 h drying in high vacuum at $65^\circ\text{C}$	14.52	$9.8\sim 10.1$

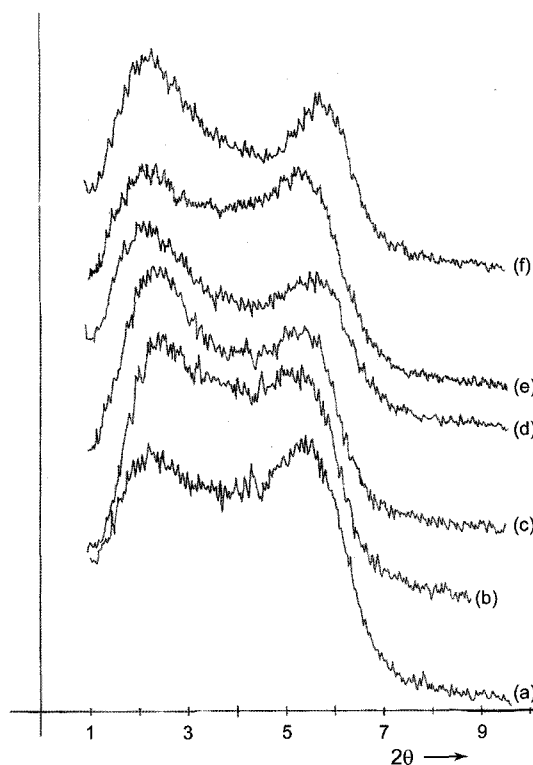


**Fig. 2.** X-ray diffraction patterns of [TEACOOH]-Montmorillonite with  $\epsilon$ -caprolactone; (a) [TEACOOH]-Mont as a starting material, (b) After intercalation of  $\epsilon$ -caprolactone into [TEACOOH]-Mont, (c) After drying of (b) in high vacuum right after the exchange reaction, and (d) After extraction with methanol and following drying in high vacuum of (b)

starting material, the organophilic [TEACOOH]-Montmorillonite intercalations complex. This suggests that the caprolactone is successfully intercalated into the layer of [TEACOOH]-Montmorillonite. However, from Fig. 2, the XRD patterns obtained after drying in a high vacuum directly after the cation exchange reaction, after the extraction with methanol and the subsequent drying in the high vacuum of  $10^{-3}$  torr at  $65^\circ\text{C}$  for 24 h, are shown to be nearly identical to those of the starting material, the organophilic [TEACOOH]-Montmorillonite intercalations complex. This suggests that the intercalated  $\epsilon$ -caprolactone between the layers of [TEACOOH]-Montmorillonite were extensively removed again from the layers again.

### 3.2. Polycondensation Reaction

In order to determine if the polymerization of  $\epsilon$ -caprolac-



**Fig. 3.** X-ray diffraction patterns of [TEACOOH]-Montmorillonite with  $\epsilon$ -caprolactone after polymerization; (a) At  $220^\circ\text{C}$  for 48 h, (b) After extraction with methanol and following drying in high vacuum of (a), (c) At  $230^\circ\text{C}$  for 48 h, (d) After extraction with methanol and following drying in high vacuum of (c), (e) At  $240^\circ\text{C}$  for 48 h, and (f) After extraction with methanol and following drying in high vacuum of (e).

tone in the layers of [TEACOOH]-Montmorillonite was successfully performed, the sample after polymerization was treated in a high vacuum at  $65^\circ\text{C}$  for 24 h. Under these conditions, the unreacted  $\epsilon$ -caprolactone, which is only intercalated into the silicate layers, will be removed from the layers again and the basal spacing will fall to approximately  $14.5 \text{ \AA}$ , which is the same value for the starting material, [TEACOOH]-Montmorillonite dried in the high vacuum. Independent of this procedure, the extraction analyses of the samples were performed with the solvents in which only the monomer or small oligomers are soluble, but not the polymer. The results measured via X-ray diffractometry are shown in Table 2 and Fig. 3.

The results shown in Table 2 and the X-ray diffraction patterns in Fig. 2 show that  $\epsilon$ -caprolactone was almost fully

**Table 2.** Results of Polymerization of  $\epsilon$ -Caprolactone in [TEACOOH]-Mont

Sample treatment	Basal spacings ( $\text{\AA}$ ) after reaction of [TEACOOH]-Mont. with monomer before polymerization	Basal spacings ( $\text{\AA}$ ) for 48 h at		
		$220^\circ\text{C}$	$230^\circ\text{C}$	$240^\circ\text{C}$
Starting material for polymerization	50.72			
After polymerization		37.12	38.15	39.02
After extraction with methanol and dried in high vacuum at $65^\circ\text{C}$ , 24 h	14.53	34.24	35.62	37.34

removed from the layers of [TEACOOH]-Montmorillonite. This is true if caprolactone was not polymerized in the layers, dried at 65°C for 24 h in a high vacuum directly after the intercalation reaction (Fig. 2(c)) and after extraction with a solvent (in this case methanol) (Fig. 2(d)). However, from the results shown in Table 2 and Fig. 3 it can be observed that the  $\epsilon$ -caprolactone was not removed from the layers after the polymerization. This suggests that the polymerization of  $\epsilon$ -caprolactone was successfully performed between the layers of [TEACOOH]-Montmorillonite.

In the second column of Table 2, the basal spacings of the reaction product, [TEACOOH]-Caprolactone-Montmorillonites, which was synthesized by the intercalation reaction of  $\epsilon$ -caprolactone into the layers of [TEACOOH]-Montmorillonite and will be used as a starting material for the polymerization of the organic monomer are summarized. The basal spacing of [TEACOOH]-Caprolactone-Montmorillonite before polymerization was 50.72 Å; this was reduced to 14.53 Å after extraction with the solvent methanol in which the monomer is soluble following drying in a high vacuum at 65°C for 24 h. This is caused by the removal of all  $\epsilon$ -caprolactone from the layers in a high vacuum by vaporization.

In the next column of the Table 2, the basal spacings of the products obtained after polymerization for 48 h at 220°C, 230°C, and 240°C are summarized. From the results shown in Table 2, it is clear that in every case the basal spacing increased with the reaction temperature. After polymerization at 220°C the basal spacing is 37.12 Å, while the basal spacings obtained after polymerization at 230°C and at 240°C are 38.15 Å and 39.02 Å, respectively. After extraction with methanol and following drying in a high vacuum at 65°C for 24 h, the basal spacings fell to 34.24 Å, 35.62 Å, and 37.34 Å for 220°C, 230°C, and 240°C, respectively.

While the basal spacing obtained before polymerization were 14.53 Å as nearly all of the intercalated monomer was removed from the layers, the measurement after extraction of the polymerized sample with solvent (methanol), in which the monomer is soluble following drying at 65°C for 24 h in a high vacuum, are higher than 34 Å in all cases. This shows that polymerization proceeded successfully. In general, the results of Table 2 show that the higher the basal spacing becomes, the higher the reaction temperature is.

Comparing Fig. 2 with Fig. 3, it is evident that the X-ray peaks obtained after polymerization are not sharp and are far broader 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 must 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

For a more precise investigating and analysis of the poly-

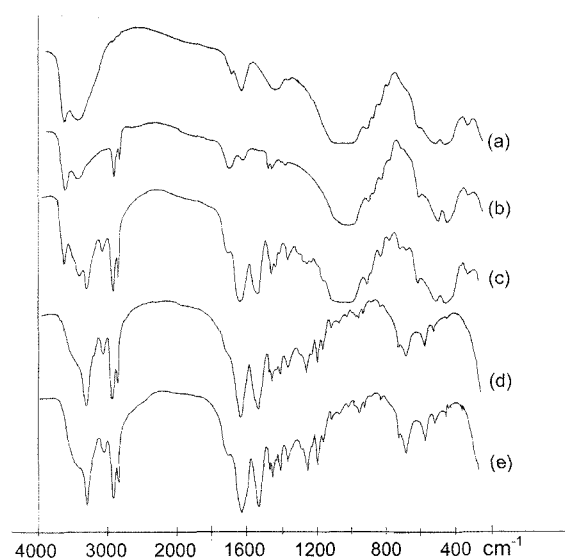


Fig. 4. IR-spectrums for (a) Na-Montmorillonite, (b) [TEACOOH]-Montmorillonite (c) [TEACOOH]-Polycaprolactone-Montmorillonite, polymerized for 48 h at 240°C extraction with methanol and dried in high vacuum at 65°C for 24 h, (d) Polymer, isolated from the interlayer space of montmorillonite (Original polymerization in interlayer space at 240°C for 48 h, extraction with methanol, then isolated by the  $\text{NH}_4[\text{HF}_2]$ -process), and (e) Polycaprolactone, synthesized without montmorillonite, after extraction with water and dried in a high vacuum at 65°C for 24 h.

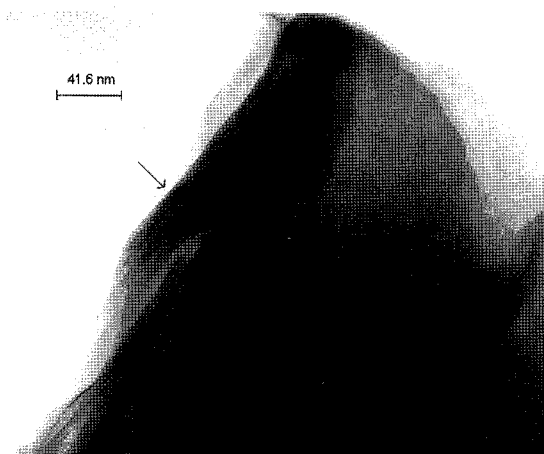
mer products, the polymerized sample was separated from the silicate layers. However, as can be observed from the results of the extraction with the solvent, it was not possible to separate the polymerized product from the interlamellar space by extraction with solvent. It was also not possible to isolate the polymer ion existing between the layers by the cation exchange reaction, as ions with a high molecular weight are linked more strongly with montmorillonite in the interlamellar space than those with a low molecular weight. Therefore, in order to separate it, a  $\text{NH}_4[\text{HF}_2]$ -solution was used to decompose the silicate lattice. The isolated sample was then analyzed with an X-ray diffractometer and IR-spectrometer, and the results are shown in Fig. 5.

### 3.4. IR-Analysis

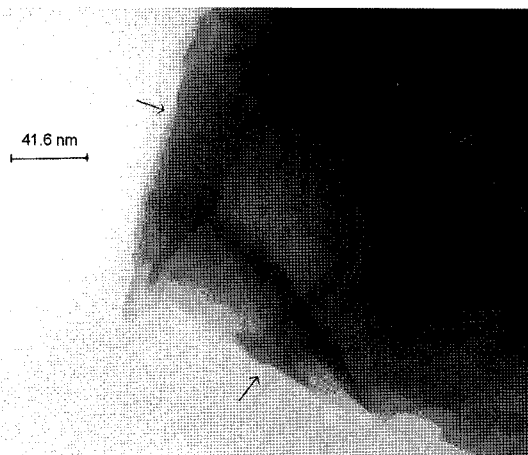
The results of IR-analyses for each sample are presented in Fig. 4. The IR-spectrum for Na-Montmorillonite is demonstrated in Fig. 4(a) and includes somewhat characteristic broad peaks. Fig. 4(b) shows the IR-spectrum for [TEACOOH]-Montmorillonite with the cation between the layers. In this spectrum, sharp peaks are shown in the region from 2830 to 2920  $\text{cm}^{-1}$ , from 1470-1530  $\text{cm}^{-1}$  and at 1750  $\text{cm}^{-1}$  which did not exist in the spectrum for Na-Montmorillonite and which were derived from the organic cation intercalated between the layers.

Fig. 4(c) shows the IR-spectrum for the [TEACOOH]-Polycaprolactone-Montmorillonite sample synthesized by the polycondensation reaction of  $\epsilon$ -caprolactone between the lay-

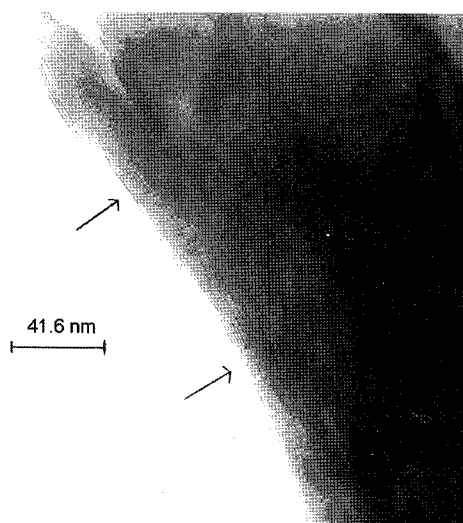
ers of the [TEACOOH]-Montmorillonite intercalations complex, as extracted with a methanol solvent to remove the caprolactone that was not polymerized, and then dried at 65°C for 24 h in a high vacuum. In this case, additional



(a) 220°C



(b) 230°C



(c) 240°C

Fig. 5. TEM pictures of the montmorillonite/polycaprolactone nanocomposites.

sharp peaks can be seen.

In Fig. 4(d), the IR-spectrum for the sample isolated from the interlayer spaces of montmorillonite after decomposition of [TEACOOH]-Polycaprolactone-Montmorillonite with  $\text{NH}_4[\text{HF}_2]$  is shown. For comparison, the spectrum for the polymer synthesized by the reaction of  $\epsilon$ -caprolactone with [TEACOOH]-Montmorillonite without montmorillonite is shown in Fig. 4(e). Comparing Fig. 4(d) with Fig. 4(e), it becomes clear that both polymers that were synthesized under different reaction conditions are the same 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 [TEACOOH]-Mont occurred.

### 3.5. Transmission Electronic Microscopy (TEM)

It is very interesting to investigate the altered appearance of the clay (montmorillonite) mineral, which is used as a reinforcement for the polymer matrix after the polymerization reaction of [TEACOOH]- $\epsilon$ -caprolactone-Montmorillonite. Thus, the polymerized product was investigated with a transmission electronic microscope (Fig. 5). From Fig. 5, a repeating arrangement of the layers of the reinforced montmorillonite in the polymer matrix of montmorillonite/polycaprolactone nanocomposites can be seen.

## 4. Conclusions

In this study, an attempt was made to polymerize the monomer,  $\epsilon$ -caprolactone, between the layers of the [TEACOOH]-Montmorillonite intercalations complex to achieve a [TEACOOH]-Polycaprolactone-Montmorillonite nanocomposite in which the inorganic material (montmorillonite) and the organic material (polycaprolactone) are chemically linked. The following results were observed:

1. The basal spacings for the samples obtained after polymerization range from 34.24 Å to 37.34 Å under a dried condition in a high vacuum after extraction with methanol, while those for the samples before polymerization lie between 14.53 Å under the same conditions.

2. In particular, the condition in which the higher the basal spacing became, the higher the reaction temperature became was observed.

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

4. Comparing the IR-spectrum for the sample separated from the layers of [TEACOOH]-Mont after polymerization of  $\epsilon$ -caprolactone between the layers of [TEACOOH]-Mont with that of the polymer synthesized by the reaction of  $\epsilon$ -caprolactone only with the organic cation, [TEACOOH] Br, without montmorillonite, it is obvious that both polymers synthesized under the different reaction conditions are the

same compound.

5. Repeating arrangements of the layers of 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 layer spaces of the [TEACOOH]-Montmorillonite intercalations complex.

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