

in situ 중합을 통한 나일론 6-PEG 랜덤공중합체/점토 나노복합체의 합성 및 물성

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Synthesis and Properties of Nylon 6/PEG Random Block Copolymer/Clay Nanocomposite via *in situ* Polymerization

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1. INTRODUCTION

There has been extensive interest in the development of new nanocomposites. One kind of these systems is the hybrid based on organic polymers and inorganic minerals consisting of layered silicates. Some properties like stiffness, strength, barrier properties, thermal, and oxidative stability can be improved by the presence of the filler in the polymeric matrix[1]. It is reported that, in the nylon 6/clay nanocomposites, the modulus is increased, but impact strength and elongation at break are drastically decreased. To solve these problems, we tried to synthesize new nanocomposites based on nylon 6 and clay using polyethylene glycol diamine as a soft segment via *in situ* condensation polymerization. Pure sodium montmorillonite and surface modified montmorillonite with 12-aminododecanoic acid were used as nanoparticle precursors and 6-aminocaproic acid as a polymerization catalyst.

2. EXPERIMENTAL

Nylon 6 nanocomposites and nylon 6 random copolymer nanocomposites (N6RCN) were synthesized in a 500 ml autoclave. Montmorillonite modified with 12-aminododecanoic acid (ADA) and sodium montmorillonite (MMT) provided by Nanocor, were used as nanoparticles. The clay was dispersed on the weight of 2, 3.5, and 5% of ϵ -caprolactam (CL) in CL at 90°C for 1.5 h. The N6RCN nanocomposites were synthesized adding polyethylene glycol diamine (JeffamineED-2001, Texaco Chemical, USA) as a soft segment. The polymerization was carried out at 260°C for 6 h under the atmosphere of nitrogen using 6-aminocaproic acid as a catalyst (See Fig.1). Before finishing the polymerization, vacuum was applied to remove the

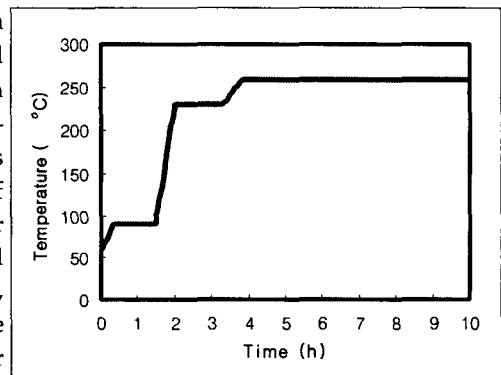


Fig.1. Temperature profile during *in situ* polymerization.

residual water in the polymer. The polymer products were extruded and made into a form of chip.

X-ray diffraction measurement was used to estimate the degree of exfoliation of clay. Scanning electronic microscopy (SEM) was used to analyze the morphology and DSC measurement was used to analyze the crystallization and melting behavior of the specimens.

3. RESULTS AND DISCUSSION

3.1 XRD

The determination of intercalation or exfoliation can be determined using XRD results. In Fig.2 the diffraction pattern curves are presented for nylon 6 random copolymer nanocomposites using 5% of Jeffamine ED-2001 and 2, 3.5 and 5 wt% of clay.

The ADA-clay presented a diffraction peak at $2\theta=5^\circ$. The nylon 6 random copolymer nanocomposites with ADA-clay do not show the diffraction peak of ADA-clay. This suggests that the silicate layers of ADA-clay can be exfoliated during polymerization[2]. In MMT nanocomposites, one peak at 4.5° is observed. This may be related with only intercalation of the clay. These results were also supported by SEM results.

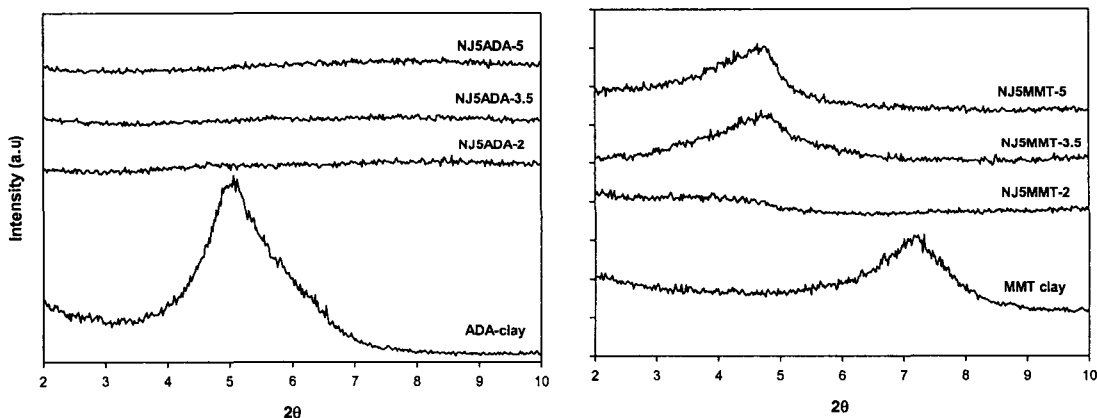


Fig.2. Diffraction patterns for nylon 6 random copolymer nanocomposites.

3.2 Thermal transitions

DSC results are summarized in Table 1. Jeffamine presents melting and crystallization temperatures around 46.7°C and 19°C , respectively. Nylon 6 nanocomposites with 5% of Jeffamine, only the melting point of nylon 6 is observed. The absence of melting point of Jeffamine indicates the formation of random copolymer. The nylon 6 with 5% of soft segment presents lower melting and crystallization temperature than nylon 6, due to the presence of Jeffamine destroyed the crystalline chains of the rigid segment (nylon 6) [3]. With the addition of clay, both melt-crystallization temperature and melting temperatures are shifted to a lower temperature. All nanocomposites presented two melting peaks around 221°C and 210°C , which correspond to the melting of the α and γ crystalline structures, respectively. This indicates that the presence of soft segment does not permit good interactions between nylon 6 chains and clay.

Table I. Results of T_{cm} , T_m and ΔH_f obtained from DSC.

	Clay (wt%)	T_{cm} ($^{\circ}C$)	ΔH_c (J/g)	$T_m(^{\circ}C)$ $v_{phase/a}$ phase	ΔH_f (J/g)
Nylon 6		185.5	54.6	^{sn} 213/221	31.6
Jeffamine		19	-	46.7	-
NJEF-5		182.01	54.9	^{sn} 213/221	21.97
	2	182.2	45.8	^{sn} 210/220	41.3
NJ5ADA	3.5	180.2	48.2	^{sn} 213/220	38.27
	5	178.2	42.1	212/219 ^{sn}	29.32
	2	183.5	49	213/220	35.73
NJ5MMT	3.5	182	49	213/220	33.31
	5	182	43.6	213/219.9	27.67

sh : shoulder

3.3 SEM

SEM images are shown in Fig. 3 for the samples with 5% of ADA- and MMT-clay by weight. These results accord with the XRD results. The mechanical properties presented better results for ADA samples. These materials have higher yield stress, higher initial modulus, and lower strain at break than MMT samples. With increasing the content of Jeffamine, as a soft segment, the modulus and the yield stress decrease.

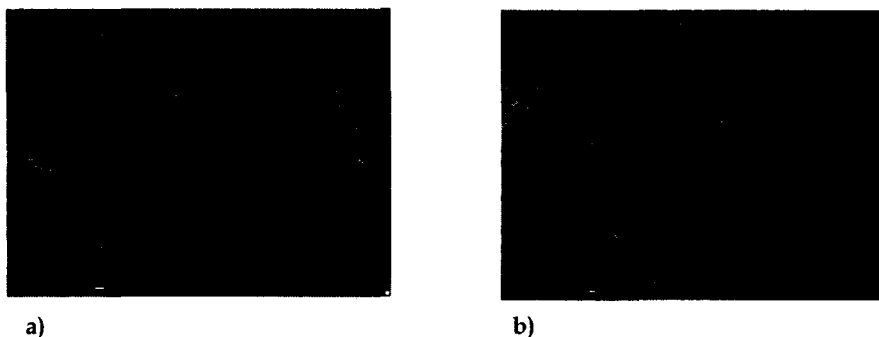


Fig.3. SEM micrograph of a) 5% of ADA-clay and b) 5% of MMT-clay in nylon 6 random copolymer nanocomposites.

4. CONCLUSION

Nylon 6 nanocomposites with Jeffamine as a soft segment were synthesized by *in situ* polymerization. SEM microscopy and X-ray diffraction indicate that the ADA-clay is well dispersed in the polymer matrix. In MMT case, there are only intercalation with the polymer. The presence of Jeffamine produced a random copolymer during the polymerization, decreasing the crystallinity of nylon 6.

REFERENCES

- 1) J.W. Cho and D.R. Paul, *Polymer*, **42**, 1083 (2001).
- 2) A. Ranade and N. Anne, *Polymer*, **43**, 3759 (2002).
- 3) K. Sakurai and G. Amador, *Polymer*, **17**, 4089 (1998).

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