Poly (ε-Caprolactam)–Poly(Butadiene-co-Acrylonitrile) Block Copolymers. I. Synthesis, Characterization, Mechanical Properties, and Morphology

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SYNOPSIS

Poly(ε-caprolactam)–poly(butadiene-co-acrylonitrile) block copolymers have been synthesized that were suitable for the pultrusion process. The effects of amine-terminated butadiene acrylonitrile copolymer (ATBN) content on copolymerization rate, conversion, crystallization behaviors, and mechanical properties and morphology of NY 6–ATBN copolymers were investigated. The conversion was over 90% and the copolymerization was completed within 3 min (up to 20 wt % ATBN) at 145–165°C. The higher the [MgBr — CPL] (ε-caprolactam magnesium bromide) initiator concentration, the lower the molecular weight [or intrinsic viscosity (IV)] of the copolymers and the less the copolymerization time. Relationships among mechanical properties, morphology, and structure of copolymers have been studied. The notched Izod impact strength of the NY 6–ATBN copolymers (> 10.5 wt % ATBN) increased more than 10-fold, while the flexural modulus only reduced 10%. Transmission electron micrographs showed that ATBN rubber particle size changed slightly with ATBN content, but interparticle distance (T) decreased with increasing ATBN content. As T decreased, the ductility of the copolymers increased. When ATBN content reached 10.5–13 wt % ($T = 0.32$–0.45 μm), the copolymers showed a very high ductile behavior. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The resins used most for the pultrusion process are thermoset resins (e.g., unsaturated polyester, epoxy and phenolic resin, etc.). However, thermoplastic composites possess the following advantages: higher degree of processing freedom (reformability, repairability, and good wetting ability), faster production rate, good toughness, scrap can be reused, and free from solvent pollution problems. Hence, there has been increasing interest in research on, and applications of, thermoplastic pultrusion[1-4] in recent years. However, there are some difficulties in thermoplastic pultrusion, one of the major problems being poor fiber wet-out by resin owing to the very high viscosity of the thermoplastic resins. Considerable research[1-6] has been devoted to solve this

problem but seldom successfully. *In situ* polymerization offers one approach to achieve good fiber wet-out by directly converting monomers or prepolymer to polymer in the pultrusion die.[7,8] The very low viscosity of the reactive precursor enables excellent fiber wet-out.

Many studies describe the synthesis of rubber-toughened Nylon 6,[9-11] however, either solvent is used in these studies or polymerization time is too long, consequently, they are not suitable for pultrusion. In recent years, the resin system used in rubber-toughened Nylon 6 reaction injection molding[12-15] (RIM) may be able to meet the requirements for pultrusion. The majority of resin systems used in RIM have been copolymers of polypropylene oxide or polybutadiene, but a serious phase separation may occur. In this study, the polar acrylonitrile in amine-terminated butadiene acrylonitrile copolymer (ATBN) is used to provide sufficient solubility of the propagating polymers in ε-caprolactam.

The aims of this work are to study the effect of

reaction parameters on the conversion efficiency of copolymerization and on molecular weight of the copolymers that can be suitable for the pultrusion process, and to study the effect of ATBN content on copolymerization rate and crystallization behavior. This study also investigates the static and dynamic mechanical properties of NY 6–ATBN copolymer, especially the improvement in toughness by incorporation of ATBN liquid rubber. Results show that the notched Izod impact strength of the NY 6–ATBN copolymers (> 10.5 wt % ATBN) increases more than 10-fold, while the flexural modulus only reduces by 10%. Relationships among morphology [by transmission electron micrographs (TEM)], mechanical properties, and structure of copolymers have been established.

EXPERIMENTAL

Materials

The materials used in this study are listed, with properties and sources, in Table I. Terephthaloyl biscaprolactam (TBC) was prepared from terephthaloyl dichloride and ε-caprolactam.[16] The initiator, ε-caprolactam magnesium bromide (MgBr— CPL) was synthesized from ethyl magnesium bromide and ε-caprolactam, the former being dissolved in diethyl ether and added gradually into an excess of molten ε-caprolactam with stirring under nitrogen atmosphere at 80°C.

Copolymerization

ε-Caprolactam in a glass reactor was dried with stirring under nitrogen, which was purified by silica gel molecular sieve, P_2O_5 (to remove moisture) and BTS catalyst (from Merck Co., to remove O_2). After drying, the moisture content was below 200 ppm, which was determined by a Karl-Fisher titrator. The liquid rubber ATBN (from BF Goodrich Co.) and TBC are equimolar with respect to the end-group content of ATBN and were added to the dried ε-caprolactam with stirring and kept at 90°C for 2 h. The amine end groups of ATBN were then blocked by TBC to form a polymeric activator. This activator mixed with ε-caprolactam was then poured into ampoules. The ampoules were degassed under vacuum for 1 h at 80°C. MgBr–CPL initiator with excess CPL at 90°C was added into ampoules that contained activator and CPL by syringe. After MgBr–CPL initiator was added, the ampoules were transferred to an oil bath at copolymerization temperature (145/155/165°C). The solid NY 6–ATBN copolymers were ground to less than 1 mm in diameter.

Characterization of Copolymers

1. Conversion of copolymerization: The polymerization products were fractioned into high polymer and a methanol-soluble fraction (containing residual CPL monomer, oligomers) by methanol extraction in a Soxhlet apparatus for 48 h (oil bath at 130°C).

Table I   Materials Used in This Study

Material	Specification	Supplier
ε-Caprolactam (CPL)	MW = 113.2 Recrystallized in cyclohexane	China petroleum Co., Taiwan
Amine-terminated butadiene acrylonitrile copolymer (ATBN)	Hycar 1300 × 16 Amine equiv. wt = 900 Acrylonitrile content 16 wt %	BF Goodrich Co., U.S.A.
Terephthaloyl dichloride	MW = 203 Purity > 98%	Merck Co., U.S.A.
Terephthaloyl biscaprolactam (TBC)	MW = 244	Synthesized in this study
Ethyl magnesium bromide	MW = 133.3, dissolved in diethyl ether (3M)	Tokyo Kasei Kogyo Co., Japan
ε-Caprolactam magnesium bromide (MgBr–CPL)	MW = 216	Synthesized in this study
Methanol	L.C. grade Purity > 99.7%	Alps Chem. Co., Taiwan
m-Cresol	Purity > 99.4%	Janssen Co., Belgium
2,2,2-Trifluoroethanol	Purity > 99%	Janssen Co., Belgium
BTS Catalyst	Consists of 30% copper fixed in an inert support	Merck Co., U.S.A.

2. Intrinsic viscosity was measured in *m*-cresol at 30°C.
3. Copolymerization time: As the copolymerization proceeded, the viscosity of reaction mixture increased rapidly, until the stirring bar cannot rotate anymore. The mixture was then watched carefully to see the onset of solidification of the copolymers by phase separation on a cloud point formed in the ampoule. The copolymerization time is defined as the time required to form a cloud point.[17]
4. Crystallization behavior was studied by using a Seiko 5200 differential scanning calorimeter (DSC) with the following procedure: The sample (about 5 mg) was heated up to 250°C under a nitrogen atmosphere and kept at this temperature for 10 min and then was cooling at 10°C/min to 60°C.
5. IR spectra were recorded on a Perkin-Elmer 842 Spectrophotometer. Films were cast from the 1 wt % solution of copolymers in trifluoro ethanol on a plain glass.

Mechanical Properties of Copolymers

In order to obtain the specimens for mechanical properties measurement of the copolymers, two sheets (160 × 130 × 3.2 and 160 × 130 × 6.4 mm) were made by copolymerization casting in a well-sealed mold. After demolding at 80–90°C, the sheets were immediately dipped into a silicone oil bath to prevent water take-up. Specimens were cut from the sheets when they had cooled to room temperature.

1. Flexural strength and modulus were measured following ATSM D-790 with an Instron 4201 universal testing machine. The sample dimensions were 127 × 12.7 × 6.4 mm (length × width × thickness), the span was 10 cm and the crosshead speed was 5 mm/min.
2. The dynamic mechanical properties were measured with a DuPont dynamic mechanical analyzer (DMA) at a frequency of 1 Hz and a heating rate of 3°C/min. The sample dimensions were 50 × 10 × 3.2 mm.
3. Notched Izod impact strength was measured following ASTM D-256 with a TMI43-1 impact tester from Testing Machines Inc., U.S.A. Thickness of sample was 3.2 mm.

Transmission Electron Microscopy (TEM)

Thin films (about 0.1 μm) were prepared by casting the solution containing 1% copolymer (in *m*-cresol)

on water. The thin films were picked up by a 200-mesh copper grid. After drying, the grid was kept in a 4% aqueous solution of OsO_4 for 2 h. A Jeol JEM-100 CXII transmission electron microscope operated at 100 kV was used to examine the samples.

RESULTS AND DISCUSSION

Study on the Copolymerization and Analyze the Structure of Copolymer

In order to synthesize a modified Nylon 6 that is suitable for pultrusion, the rate of copolymerization must be very fast (i.e., reaction completed within 3 min). In this study, telechelic copolymers of butadiene with acrylonitrile terminated by amine group (ATBN) were converted into a polymeric activator, i.e., polymers carrying groups capable of acting as growth centers for anionic polymerization of ε-caprolactam. The reaction of synthesis of the polymeric activator is[18]

$$\text{.................} \quad (1)$$
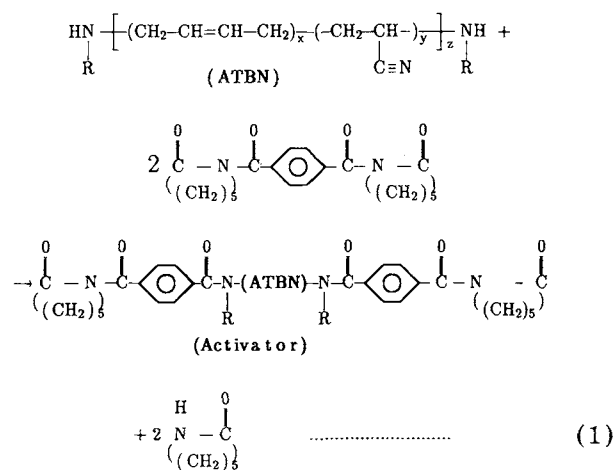
The copolymerization occurs rapidly when this activator is mixed with initiator (MgBr–CPL) and ε-caprolactam.

$$\text{............} \quad (2)$$
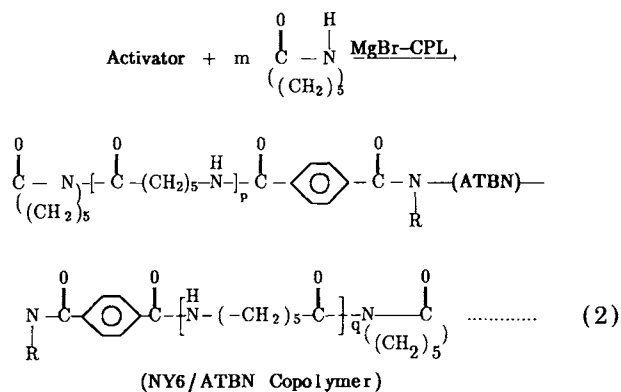
(NY6/ATBN Copolymer)

Figure 1 illustrates the IR spectrum of the NY 6–ATBN copolymer, which can be identified from the main absorption peaks as follows[19]:

1. 3100–3500 cm^{-1}: N—H stretch
2. 2850–3000 cm^{-1}: C—H (alkane) stretch
3. 2240–2260 cm^{-1}: C≡N stretch
4. 1640–1670 cm^{-1}: C=O (amide) stretch
5. 1550–1640 cm^{-1}: N—H (amide) bending
6. 1000–1350 cm^{-1}: C—N (amide) stretch
7. 960–980 cm^{-1}: C—H (alkene, trans) out of plane bending
8. 665–730 cm^{-1}: C—H (alkene, cis) out of plane bending

Analysis of the IR spectrum confirms the structure of NY 6–ATBN copolymer as shown in equation (2).

The effect of initiator concentration [MgBr–CPL] on the intrinsic viscosity (IV) and conversion (*f*) of NY 6–ATBN copolymers is shown in Figure 2. The higher the initiator concentration the lower the IV value (i.e., the lower the molecular weight) of copolymers. The initiator reacted with activator to form a "growth center" of anionic polymerization

of ε-caprolactam, hence, the more the initiator, the more the growth center. During the copolymerization process, the monomers (CPL) were consumed very fast (usually within a few minutes or seconds) by the growth centers. The more the growth centers the fewer the number of monomers on each copolymer chain at the end of copolymerization, hence the IV of the copolymer will be lower. On the other hand, the more the growth centers, the higher the possibility that monomer can react with growth centers. This may explain why the conversion increased with initiator concentration. However, when MgBr–CPL concentration is more than 1.25 mol % (based on CPL), the conversion will not increase with increasing MgBr—CPL content.

Figure 3 illustrates the effect of MgBr–CPL concentration and reaction temperature on the copolymerization time (t_p) of NY 6–ATBN copolymers. The t_p decreases with increasing MgBr–CPL and reaction temperature. One of the requirements of copolymers to be utilized in the pultrusion is t_p < 180 s, hence the suitable MgBr–CPL concentration is 1.0–1.5 mol % (based on CPL) at the die temperature 145–165°C for 13 wt % ATBN copolymers.
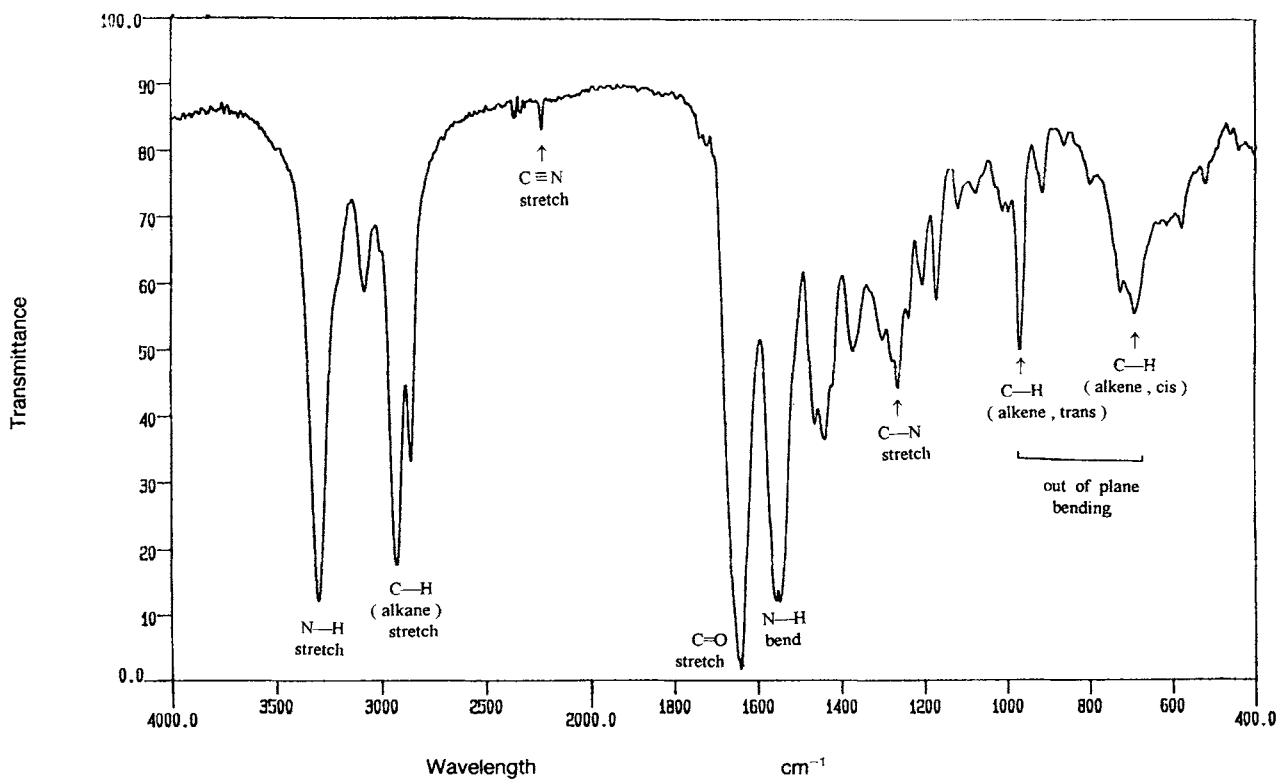

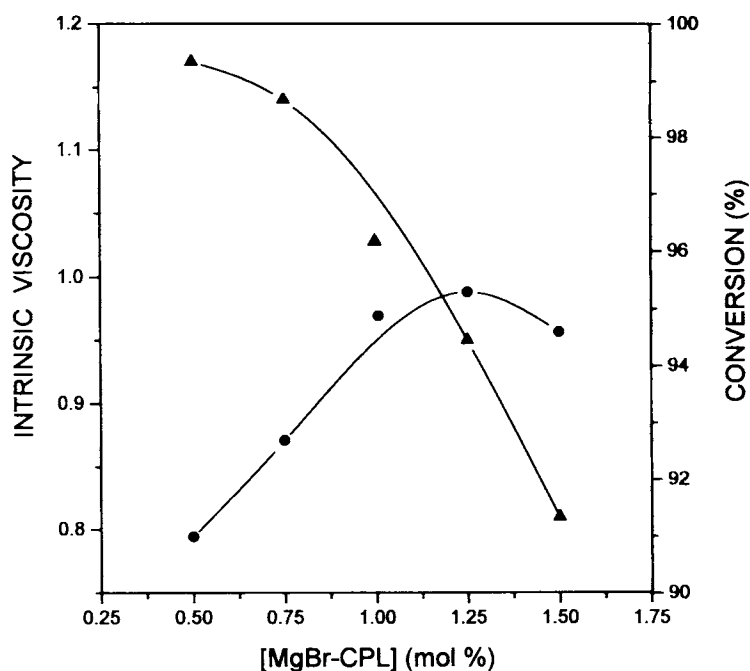**Figure 1** IR spectrum of NY 6–ATBN copolymer (22.9 wt % ATBN).

Figure 2   Effect of initiator concentration on the (▲) intrinsic viscosity and (●) conversion of NY 6–ATBN copolymer (13.5 wt % ATBN, reaction temperature 155°C).
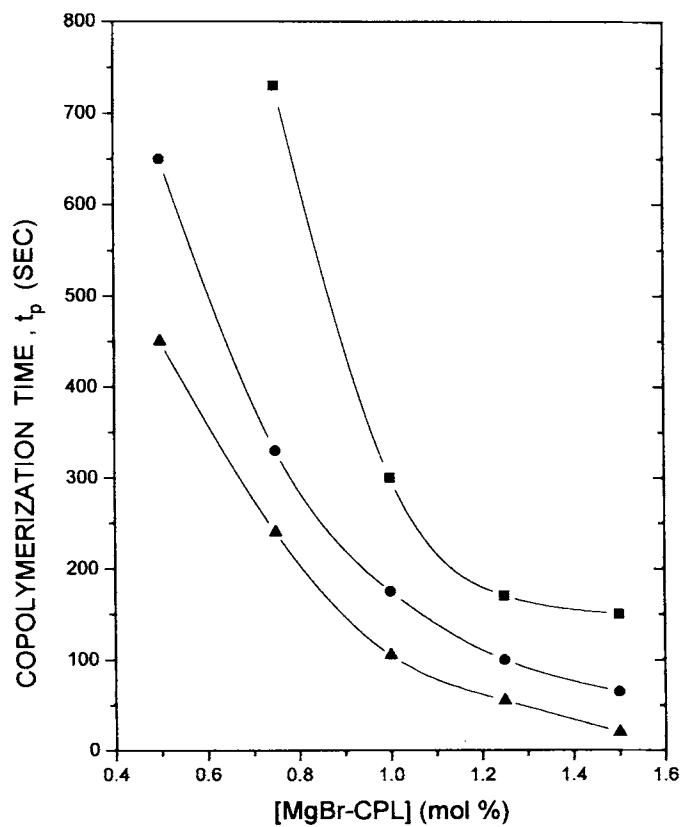

Figure 3   Effect of initiator concentration and reaction temperature [(■) 145°C, (●) 155°C, (▲) 165°C] on the copolymerization time (t_p) of NY 6–ATBN copolymers (13.5 wt % ATBN).
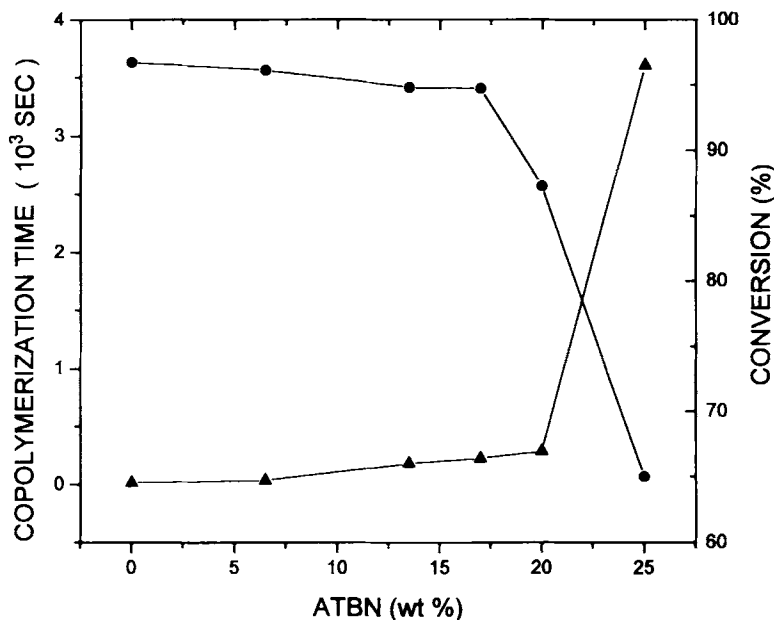
Figure 4   Effect of ATBN content on the (▲) copolymerization time and (●) conversion of NY 6-ATBN copolymers. ([MgBr-CPL] = 1.0 mol %, reaction temperature 155°C).

It can be seen from Figure 4 that ATBN retards the copolymerization rate. When ATBN is more than 20 wt %, a sharp decrease of conversion was observed. This behavior may not only be attributed to the rather small change in activator, initiator, and monomer concentration (i.e., to the dilution effect owing to the higher ATBN content), but also to the significant increase of viscosity by ATBN. The high viscosity of the liquid rubber (ATBN) leads to a higher viscosity polymerization system, and thus may reduce the diffusion rate of CPL and lower the rate and the possibility of CPL to react with the growth centers.

Crystallization Behavior

ATBN not only retards the copolymerization rate but also lowers the onset and peak temperature of crystallization when cooling (10°C/min) from the melt of NY 6-ATBN copolymers.

Table II shows the effect of ATBN content on crystallization behavior of its copolymers. The melting temperature was lowered by increasing the ATBN content. The heat of crystallization (ΔH_{cc}) and the heat of fusion (ΔH_f) were lowered by increasing ATBN content, however, when they were normalized by the actual NY 6 content (the part that contributed to crystallization), it was found that the effect of ATBN on ΔH_f and the actual crys-

tallinities (x_c/w) of copolymers are not so pronounced and x_c/w was almost constant with NY 6 content between 61.5 and 93.2 wt %, as shown in Table III. Similar results have been shown in another study[20] in which the actual crystallinities of the polyamide-polybutadiene copolymers were almost constant for NY 6 content at 70-90 wt %.

Relationships among Mechanical Properties, Morphology, and Structure of Copolymers

Both flexural strength and flexural modulus decrease with increasing ATBN content as shown in Figure

Table II   Thermal Behavior of NY 6-ATBN Copolymers

ATBN Wt %	Crystallization (Cooling)			Melting		
	Onset (°C)	Peak (°C)	ΔH_{cc} (J/g)	Onset (°C)	Peak (°C)	ΔH_f (J/g)
0.0	188.4	181.8	60.5	203.3	216.2	61.3
6.8	185.7	178.4	50.7	196.6	214.9	52.5
13.5	186.0	175.6	47.9	197.9	214.3	48.0
22.9	181.1	173.4	40.8	199.2	209.4	43.1
38.5	179.8	173.0	32.2	198.4	208.9	34.2

Table III Effect of ATBN Contents on the Crystallinity and Heat of Fusion of NY 6–ATBN Copolymers

ATBN wt %	W (NY 6)	ΔH_f (J/g)	$X_c{}^a$ (wt %)	$\Delta H_f/W$ (J/g)	X_c/W (wt %)
0.0	1.000	61.3	26.7	61.3	26.7
6.8	0.932	52.5	22.8	56.3	24.5
13.5	0.865	48.0	20.9	55.6	24.2
22.9	0.771	43.1	18.7	55.9	24.3
38.5	0.615	34.2	14.9	55.6	24.2

^{a} $X_c = \Delta H_f/\Delta H_f^\circ$, $\Delta H_f^\circ = 230$ J/g,[20] the heat of fusion of 100% crystalline Nylon 6.

5. On the other hand, notched Izod impact strength increases with ATBN content as illustrated in Figure 6. The NY 6–ATBN copolymers show significant improvement in toughness, especially when ATBN contents are more than 13 wt % for which samples are not broken under these testing condition. However, the toughness improvement decreases with lowering of temperature: When it is below 0°C, all copolymers show brittle fracture behavior.

The dynamic modulus curves from the dynamic mechanical analyzer (DMA) are summarized in

Figures 7 and 8, the storage molulus (E') and loss molulus (E'') of the copolymers are plotted as a function of temperature, respectively. The more the ATBN content in NY 6–ATBN copolymers, the less the storage modulus. The dynamic loss spectra show three peaks: a glass transition temperature (T_g) of NY 6 at 42–64°C, a glass transition temperature of ATBN[21] at about −40°C[21] and a β-transition temperature (T_β) of NY 6 at about −66°C as shown in Table IV. Incorporation of 7 wt % ATBN rubber with the Nylon 6 lowers the T_g of Nylon 6 about 20°C but changes only slightly with increasing ATBN content up to 20 wt %. This phenomenon is similar to the decrease of crystallinity of NY 6–ATBN copolymers by ATBN rubber.

The T_g of ATBN at about −40°C changes slightly with ATBN content up to 20 wt %, but the peak intensity increases apparently with increasing ATBN content. The β transition of Nylon 6 (T_β) is known to be very sensitive to absorbed water and to the low-molecular-weight amide, and has consequently been attributed to molecular motion associated with hydrogen-bonded water molecules or complexes between the water molecules and amide groups.[22] It can be seen from Figure 8 and Table IV, that the T_β of pure Nylon 6 and 7 wt % ATBN copolymer are −66 and −64°C, respectively, but T_β
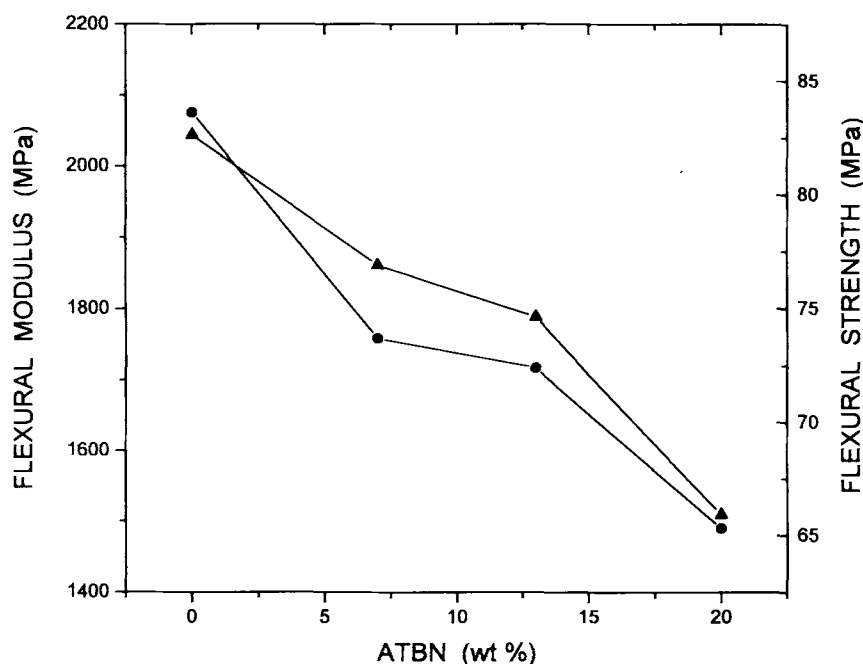

Figure 5 (▲) Flexural modulus and (●) flexural strength of NY 6–ATBN copolymers at various ATBN contents (wt %).
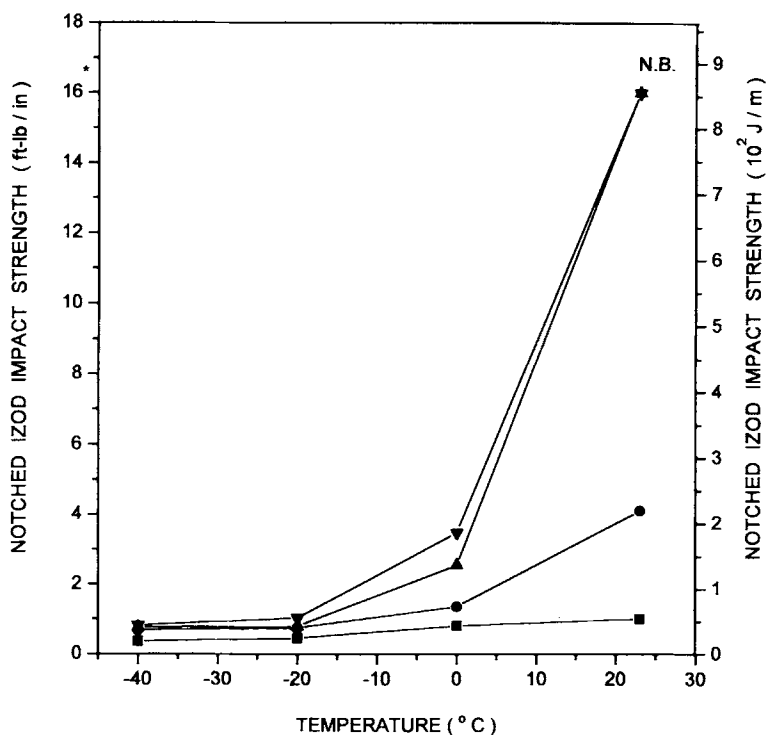
Figure 6 Notched Izod impact strength vs. temperature of NY 6–ATBN copolymers at various ATBN contents (wt %): (■) 0%, (●) 7%, (▲) 13%, (▼) 20%. *These specimens ($\frac{1}{8}$-in. thickness) are not broken (NB) after impact by a 2 ft-lb hammer, hence the impact strength is over 16 ft-lb/in.
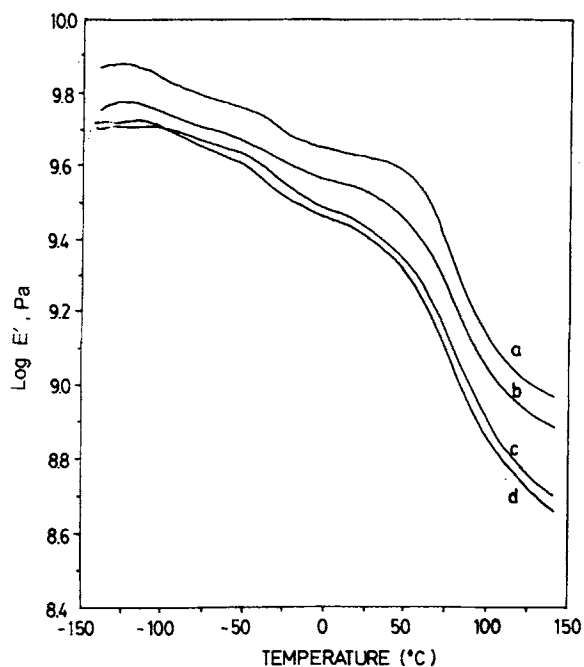
peaks of 13 and 20 wt % ATBN copolymers overlap with the T_g peaks of ATBN. There may be some kinds of interaction between the ATBN phase and
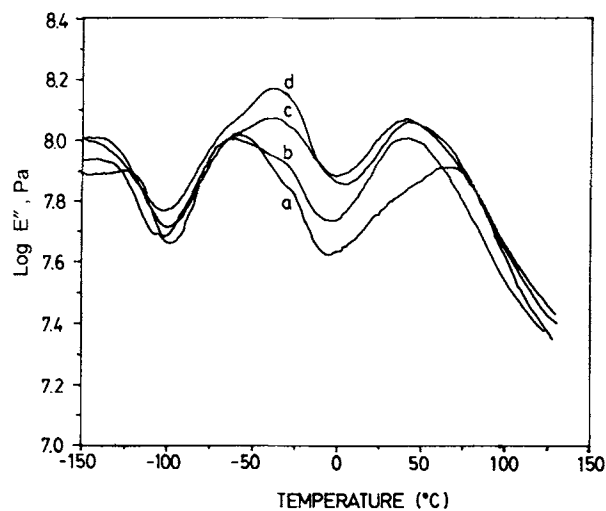

Figure 7 Storage modulus vs. temperature of NY 6–ATBN copolymers at various ATBN contents (wt %): (a) 0%, (b) 7%, (c) 13%, and (d) 20%.

Figure 8 Loss modulus vs. temperature of NY 6–ATBN copolymers at various ATBN contents (wt %): (a) 0%, (b) 7%, (c) 13%, and (d) 20%.

Table IV   Transition Temperatures of NY 6–ATBN Copolymers

ATBN (wt %)	$T_{g,NY\,6}$ (°C)	$T_{g,ATBN}$ (°C)	$T_{g,NY\,6}$ (°C)
0	−66	—	64
7	−64	—	45
13	—	−38	43
20	—	−40	42

the Nylon 6 phase. The overlap of the peaks for T_β of NY 6 and T_g of ATBN peaks and the unusual increase in peak intensity, implies some such interaction that could result in significant improvement in toughness of Nylon 6. The evidence of TEMs will further explain the improvement in toughness.

To evaluate the effectiveness of toughening of plastics, not only the improvement of toughness, but also the reduction in the mechanical properties such as flexural modulus must be taken into account. Figure 9 shows a comparison of the effectiveness of the toughened NY 6–ATBN copolymers in this

study with the toughened Nylon 6 in other research,[20] by the notched Izod impact strength vs. normalized flexural modulus. It can be observed from Figure 9 that the impact strength of the polyamide-polypropylene glycol (PPG) block copolymers and the polyamide–polybutadiene copolymers only increase significantly when the modulus is below a certain critical value. On the other hand, the blends of Nylon 6 and ethylene propylene diene monomer (EPDM) rubber with small rubber particle size and NY 6–ATBN copolymer in this study possess a combination of high toughness and high stiffness. These toughened Nylon 6 copolymers show an increase in impact strength more than 10-fold while only sacrificing 10% of modulus. According to the mechanism of toughening by an impact modifier,[23] a 10-fold or greater increase in impact strength is observed only when shear yielding of matrix occurs by the impact modifier. Energy absorption due to shear yielding requires an interparticle distance less than a certain value (T_c).[23] The morphology of NY 6–ATBN copolymers was investigated by TEM as
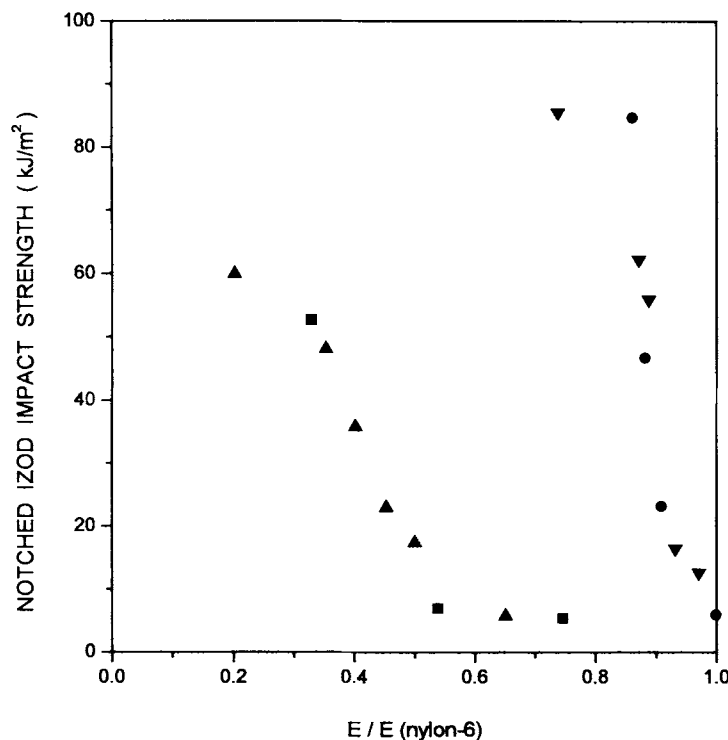

Figure 9   Notched Izod impact strength vs. normalized flexural modulus, both measured at 23°C. Comparison of (●) NY 6–ATBN copolymers in this study with toughened Nylon 6 in other research[20]: The (■) polyamide–polybutadiene copolymers, the (▲) Nylon 6-PPG block copolymers with various PPG contents (18, 20, 22, 24, 26, 30 wt % PPG), the (▼) Nylon 6-EPDM blends with various rubber contents (2, 5, 8, 10, 20 wt %), average rubber particle size ≅ 0.3 μm.
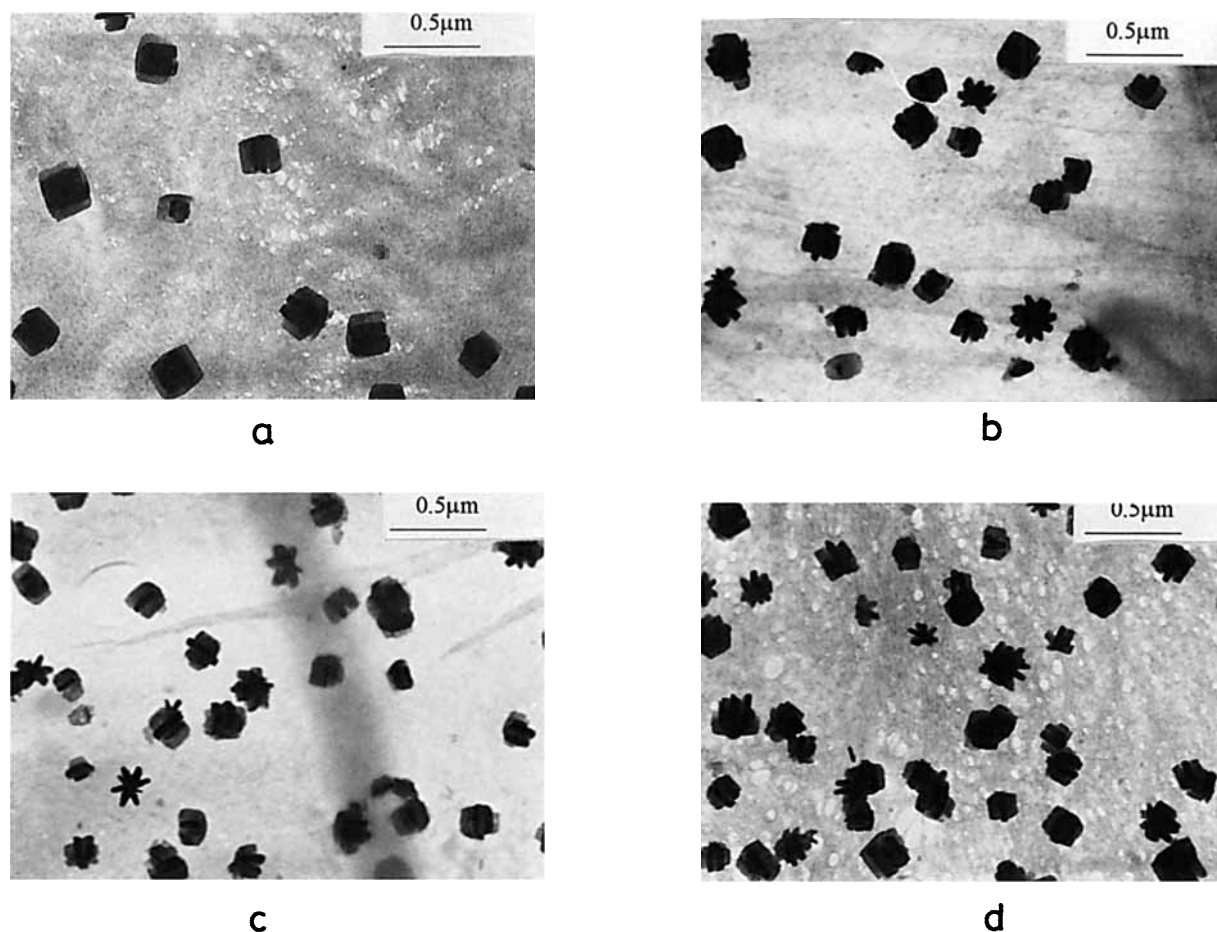
Figure 10 Transmission electron micrographs of NY 6–ATBN copolymers at various ATBN contents (wt %): (a) 7%, (b) 10.5%, (c) 13%, and (d) 20%. The dark regions are the ATBN phase, which are stained with OsO_4.

shown in Figure 10. The dark regions are due to the OsO_4 staining on polybutadiene. By measuring 300 particles on the TEM, the relationship between number-average interparticle distance (T) of NY 6–ATBN copolymer and notched Izod impact strength is obtained as illustrated in Figure 11. It can be seen from Figure 10 that the average particle diameter changes slightly with ATBN content: 7% (0.23 μm), 10.5% (0.19 μm), 13% (0.18 μm), and 20% (0.21 μm). The T_c of NY 6–ATBN is between 0.32 and 045 μm compared with $T_c = 0.304$ μm of NY 6–EPDM polyblends.[24]

CONCLUSIONS

1. The NY 6–ATBN copolymers synthesized in this study can be suitable for the pultrusion process. The conversion is 90% and the copolymerization completed within 3 min (up to 20 wt % ATBN) at 145–165°C.

2. The higher the MgBr–CPL initiator concentration, the lower the molecular weight (or IV) of the copolymers and the less the copolymerization time.

3. ATBN may retard the copolymerization and lower the conversion of NY 6–ATBN copolymers, especially when ATBN content is over 20 wt %.

4. ATBN lowers the onset and peak temperature of crystallization, when cooling from the melt, and lowers the melting point of the copolymers. However, the effect of ATBN on the normalized crystallinity is insignificant and keeps almost constant when ATBN con-
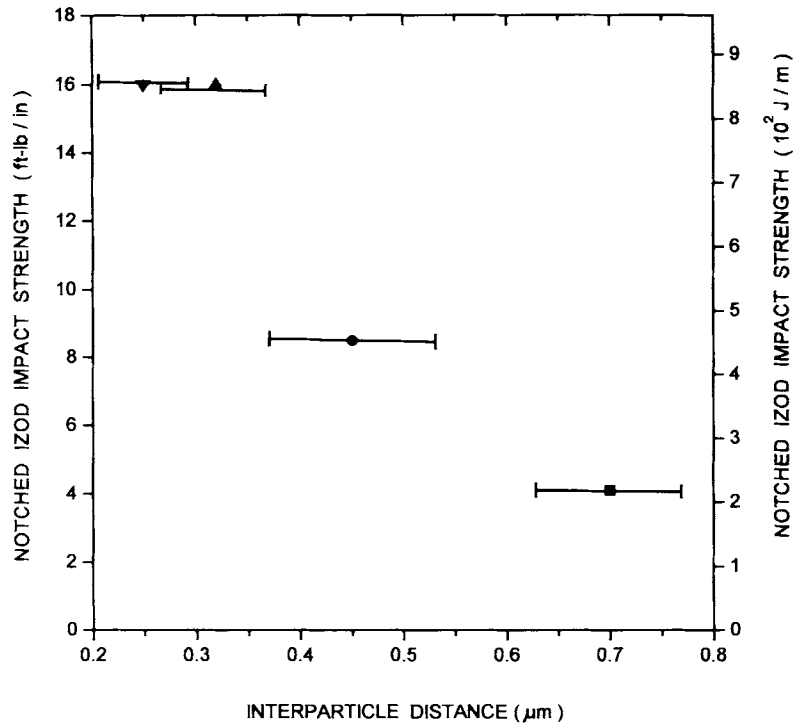
Figure 11   Notched Izod impact strength vs. interparticle distance of NY 6–ATBN co-polymers at various ATBN contents (wt %): (■) 7%, (●) 10.5%, (▲) 13%, (▼) 20%.

tent is between 6.8 and 38.5 wt % in NY 6–ATBN copolymers.

5. From the dynamic mechanical spectra, incorporation of 7 wt % ATBN rubber with Nylon 6 lowers the T_g of Nylon 6 by 20°C, but the T_g shifts slightly with increasing ATBN content up to 20 wt %. The overlap of T_β of NY 6 and T_g of ATBN peaks, and the unusual increase of peak intensity in 13 and 20 wt % ATBN copolymers, could explain the significant improvement in toughness of these Nylon 6 copolymers.

6. The notched Izod impact strength of the NY 6–ATBN copolymers (> 10.5 wt % ATBN) increases more than 10-fold, while the flexural modulus only reduces 10%. Transmission electron micrographs show that ATBN rubber particle size changes slightly with ATBN content, but interparticle distance (T) decreases with increasing ATBN content; as T decreases, the ductility of NY 6–ATBN copolymers increased. When ATBN content reaches 10.5–13 wt % ($T = 0.32$–0.45 μm), the copolymers show very high ductile behavior.

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