Effect of Diamine Addition on Structural Features and Physical Properties of Polyamide 6 Synthesized by Anionic Ring-Opening Polymerization of ε-Caprolactam

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ABSTRACT: Synthesis of ε-caprolactam in a twin screw extruder by anionic ring-opening polymerization was successfully carried out to prepare a novel nylon 6 (polyamide 6 (PA6)) containing a small amount of diamine moiety. The produced PA6 shows a remarkable improvement of the physical properties (mechanical properties as well as rheological properties). Added diamine molecules led to some structural changes in the synthesized PA6. The molar ratio of the additive (diamine) to the initiator appeared to be optimum at ca. 0.1. Although the molar mass of the PA6 has not changed significantly, less than twice the PA6 molar mass, the physical properties of the polymers produced have been markedly improved. The zero shear rate viscosity of the PA6 at the optimum diamine concentration appeared to be increased by almost 30 times that of the pure PA6. We have attributed this remarkable increase in viscosity to structural changes (branching formation during synthesis) and increased molar mass. The storage modulus at a low shear rate increased more than 100 times that of the pure PA6, but the loss modulus increased only 10-fold. This indicates that the elastic properties dominated due to the enhanced chain entanglements. In addition, the mechanical properties were significantly improved at the optimal amount of diamine reagent concentration. The elongation at break for the sample with optimum diamine addition was increased to twice that of neat PA6, whereby the tensile toughness was also doubled. Produced PA6 has a merit of processibility in the extrusion process such as a blow molding process in which stability against sagging under gravity is required and other processes in which elongational properties dominate.

INTRODUCTION

Nylon 6 (polyamide 6 (PA6)) is widely used in the film and packaging industry, the fiber industry, and the textile industry because of its outstanding physical properties such as toughness, ductility, durability, and price. 1–3 A variety of activators can polymerize an ε-caprolactam monomer within a few minutes through the anionic ring-opening polymerization (AROP) process to form PA6. They enable the in situ production of PA6 in processing operations such as reactive extrusion (REX) and reactive injection molding (RIM). 4–10

The direct ring-opening polymerization of ε-caprolactam in an extruder (a reactive extrusion process) has many obvious advantages in addition to the short reaction time so that the molecular weight of the products can be several times greater than that synthesized by conventional condensation polymerization and no by-products are formed during the synthesis. 5–7, 10 On the other hand, polymers synthesized by the condensation polymerization such as PA6 or polyesters are known to have low molecular weights, which induce quite distinctive rheological properties compared to other polymers synthesized by the free radical polymerization. They have not only a broad Newtonian viscosity plateau over a wide range of shear rates but also quite low melt viscosity. 11–14 Therefore, it has a problem to be applied in the extrusion process in which stability against sagging under gravity is required such as a blow molding process and other processes where elongational properties dominate. 14–16

However, PA6 has another useful feature: its excellent reactivity due to the reactive functional end groups. Molecules of the PA6 chain have active amine and carboxylic acid groups at the chain end that can react with other functional groups of organic/inorganic materials. 7, 8 Especially, an anhydride or epoxide group can react actively with amine end groups of PA6 chains. 9, 11, 15 Thus, a bifunctional molecule capable of reacting with two PA6 molecules can extend the molar mass of PA6. 13, 14 Some years ago, White and co-workers have extensively investigated the use of the reactive extrusion process for the synthesis of polyamides and block copolymers of poly(lactam-co-lactone). 16–18 In our previous study, we attempted to solve the rheological problems of polymers synthesized by the condensation polymerization process such as PA6 with a simple procedure, increasing the molar mass by adding a bifunctional linking agent. The linking agent can couple two chains to double its molar mass, and its viscosity can be enhanced 10 times because the shear viscosity of entangled linear polymer melts enhances with the molecular weight as $M^{1.4}$. 13 A diepoxy (4,4′-di(2,3-epoxypropyl)phenyl ben-
zote) was synthesized and mixed with a commercial PA6. The results demonstrated that the diepoxynylized nylon 6 revealed an unusual behavior as the linking agent was added. The chain relaxation dynamics were varied by several orders of magnitude by controlling the linking agent concentration. It depends on the amount of diepoxide to react with the end group of PA6 (amine group). The absolute value of the melt viscosity, η, at low frequencies increases significantly, while the shear thinning range extends over the entire shear rate. When the specimen included more molar amounts of the epoxide group than the amine group of nylon 6 (over 1:1 ratio), the melt viscosity at the peak was enhanced more than 200 times higher than that of the pure nylon 6 melt, which was attributed to the occurrence of long-chain branching without formation of a network structure (or a gel) in the melt.

In this study, we performed the synthesis of the ε-caprolactam in situ by a reactive extrusion process. ε-Caprolactam powder was premixed with a very small amount of diamine before the feeding process. The added diamine can participate in the PA6 synthesis reaction in the extruder since the anion can attack the amine group in the chain growth reaction or can only be quenched by the amine to stop the polymerization at a low conversion state or partially react with the anions to form various structures. Other researchers considered the cross-linking reaction occurrence between diepoxides and polylactams and found that the diepoxide can form block copolymers or cross-link the matrix polymers, depending on the amount of diepoxide added. In addition to the cross-linking reaction, other reactions may occur if the amount of the diepoxide is small compared to ε-caprolactam. To preclude the occurrence of the cross-linking reaction, the amount of diamine was limited to a very low level compared to the initiator (less than 0.4 mol % of the total reactants), and the appearance of a different structure than the cross-linking reaction was expected to occur. By comparing the physical properties of PA6 synthesized by AROP with and without the diamine, a clue for the puzzle of drastic change in the physical properties reported in our previous study can be found. The newly synthesized PA6 can be used in the extrusion process such as the blow molding process, which requires stability against sagging under gravity, and other processes in which elongational properties dominate.

**RESULTS AND DISCUSSION**

The mechanisms of ε-caprolactam polymerization by AROP with a terephthaloyl biscaprolactam (TBC) activator are shown in Scheme 1. TBC reacts with a sodium caprolactam anion, and the caprolactam ring is open. Then, the living anion attacks an ε-caprolactam monomer, extracts a proton, and generates a new living anion. This new anion acts as a nucleophile to open the caprolactam ring of a dimer. Thereafter, a trimer having a living anion is formed, which reacts with another ε-caprolactam monomer to increase the degree of polymerization. The chain propagation step continues until the anion is quenched. Thus, high-molecular-weight PA6 is obtained as long as the living anion is not quenched. Several investigators have reported the reaction of amine with caprolactam. Akkapeddi and Gervasi suggested that bисcaprolactam can react with the amine end group of PA6 through two possible mechanisms. The reaction mechanisms are shown in Scheme 2. Caprolactam chain end groups of polymerized PA6 can react with the diamine chain extender, forming a new PA6 repeating unit by caprolactam ring-opening or directly associating with formation of a caprolactam by-product.

In AROP of PA6 with an activator, there are some well-known side reactions that cause branching or cross-linking. In Scheme 3, it is briefly shown that possible reactions with a diamine during the polymerization can generate branches. During propagation and in the initial stage of polymerization, active anions on the living chain tend to react with activators rather than with monomers. As a result, the bifunctional activator dangles on the side position of the living PA6 chain and provides a new growth site for the production of a branched polymer. The Claisen-type condensation also produces a branched polymer chain. Stehlíček and Šebenda reported that two α-C next to the carbonyl group of polymer chain can be attacked by the lactam anion, and this new active anion could act as a branching site. The branching reaction can occur depending on the composition of the reactants, structure of activators, polymerization time, and temperature. Ricco et al. reported that high polymerization temperature and the bifunctional activator could accelerate the side reaction of PA6. Kim et al. observed more occurrences of branching and cross-linking reactions for the bifunctional activator than the monofunctional activator due to the dominant Claisen-type condensation reaction.

The viscosity molecular weights of PA6/diamine mixtures are calculated from the intrinsic viscosity, and the values are given in Table 1. Pure PA6 was well polymerized. Its molecular weight is 26,800 g/mol, which is lower than commercial PA6 resins because of the short reaction time in the laboratory-scale extruder. The molecular weight of PA6/diamine compounds was increased with a larger molar ratio of diamine to 0.1 but reduced with more diamine addition. Amine groups of PDA1 and EDA3 reacted with the caprolactam end group of PA6, affecting the whole molecular weight in two ways in the in situ polymerization. First, it increased the molecular weight by combining two PA6 chains (Scheme 2). Simultaneously, the molecular weight decreased by consumption of caprolactam and terminating the chain growth. In anionic polymerization, living anions on a growing PA6 chain transfer to other monomers, generating new living anions (Scheme 1). Subsequently, this new anion attacks the caprolactam ring located at the end of the PA6 chain. As a result, the PA6 chain length increases just as much as one repeating unit, and the anion is still alive on the PA6 chain. On the other hand, the probability that the end groups of the growing PA6 chain react with the extender increased with
increasing extender content. This means that the length of each growing chain becomes short. Until the molar ratio of the chain extender reaches 0.1, the molecular weight increases from 26,800 to 36,500 g/mol. However, if more diamines are added, the molecular weight decreased to 29,300 g/mol because the blocking effect is more predominant than the chain extension effect. However, it should be noticed that the molar mass at the diamine content of 0.1 is ca. 1.4 times that of PA6, which means that the melt viscosity is, at best, three times larger than that of PA6 if they follow the 3.4 power law. This implies that another structure is responsible for the sharp increase in viscosity. In our earlier study, we proposed that a topological change of polymer chains is the reason for the large increase in the melt viscosity.13

Figure 1 shows the dependence of the complex viscosity on the frequency at different diamine contents. The melt viscosity for PA6 does not exhibit a broad Newtonian plateau of low viscosity but a weak shear thinning behavior over the entire frequency range. This is due to the low branching during the reactive extrusion without a diamine, possibly by the Claisen-type condensation reaction because of the high extrusion...
temperature.\textsuperscript{35–37} Other PA6/diamine compounds, however, show one order higher viscosity values than neat PA6 in the whole frequency domain. This propensity is remarkable at a low frequency range, and all PA6/diamine compounds show strong shear thinning behavior. It should be noted in Figure 1a,b that the melt viscosities of in situ-polymerized PA6/diamine compounds increase with the amount of diamine up to a molar ratio of 0.1 but thereafter decrease. These phenomena are closely related to the molecular weight and chain structure of PA6 produced, as discussed later.

In our earlier study, a similar behavior was observed when a commercial PA6 was mixed with a diepoxide.\textsuperscript{13} Although the molar mass increase was only 1.5-fold, modified PA6 showed two orders higher viscosity than pure PA6. A huge increase in the melt viscosity of PA6/diepoxide indicates a topological change in the polymer chains because a slight increase in the molecular weight cannot incur such a drastic change in the viscosity if it follows the 3.4 power law ($\eta \approx M^{3.4}$). The zero shear viscosity was calculated by fitting the data using the Carreau equation with the Cox–Merz rule, $\eta(\dot{\gamma})/\eta_0 \approx (1 + (\dot{\gamma} \tau_n)^2)^{(n-1)/2}$, where $\eta_0$ is the zero shear rate viscosity, $\dot{\gamma}$ is the shear rate, $\tau_n$ is the characteristic time, and $n$ is a parameter.\textsuperscript{38} The zero shear rate viscosity has reached the highest value for the specimen containing 0.1 ratio diamine. Its zero shear rate viscosity is surprisingly ca. 30 times higher than that of neat PA6. The zero shear rate viscosity then decreased as more diamines were added. They follow almost the same trend regardless of the diamine, although the EDA3 added has a slightly higher viscosity.

Another notable change is also seen in the dynamic moduli (storage modulus ($G'$) and loss modulus ($G''$)) shown in Figure 2. The storage modulus shows the elastic solid-like behavior, while the loss modulus shows the viscous response.\textsuperscript{39} In linear polymer melts, the storage modulus is proportional to the frequency ($\omega^2$), and the loss modulus is proportional to the frequency ($\omega$) in the low-frequency region, following a linear viscoelastic (LVE) motion.\textsuperscript{40} However, the power-law dependence of $G'$ and $G''$ on the frequency becomes weaker with the addition of the diamine extender, deviating from the LVE movement. The loss modulus increased approximately 10-fold over that of PA6 at a molar ratio of 0.1 of the diamine, whereas the storage modulus increased 30 times over that of neat nylon 6 at a low frequency. After the molar ratio of 0.1, both moduli decreased similar to the change in the melt viscosity. It should also be noted that the storage modulus is higher than the loss modulus in all frequency ranges, which means that PA6/diamine mixtures have a more solid-like character.\textsuperscript{39,40}

To investigate the presence of cross-linking or branching, we measured the chain irregularity with a UV spectrometer. The OD$_{\text{max}}$ value of neat PA6 was 1.5, which was greatly higher than the value of a typical hydrolytic PA6, which is 0.044.\textsuperscript{29,36} All other PA6/diamine composites showed extremely high values of OD$_{\text{max}}$ beyond the UV spectrometer’s analysis range. This means that, in PA6 including diamines, there is a very high level of chain irregularity. It is known that cross-linking reactions may occur in the anionic polymerization of caprolactam if the reaction temperatures exceed 180 °C and near complete monomer conversion.\textsuperscript{31,33} However, the PA6 molecules were not significantly cross-linked for the following reasons. To clearly examine whether the PA6 and its blends were cross-linked or not, the gel content of PA6 and its mixtures was extracted with a solvent, 95% formic acid. After the extraction, there was almost nothing left. This was checked by the particle size analyzer. The results show that PA6 has a very high level of chain irregularities but only a small amount of cross-linking structures, which means that most of them are branching structures.\textsuperscript{13} Rico et al. have reported that anionically synthesized polycaprolactam has $T_g$ and $T_w$ values very close to those of hydrolytic polycaprolactam. It does not have cross-linked structures and instead exhibits a high degree of damping crystallinity and a very low content of $\gamma$ form.\textsuperscript{35} The occurrence of the cross-linking reaction cannot explain the large increase in the viscosity as well as the storage modulus since the cross-linked molecule volume is too small to change the rheological properties so eminently. Once it is cross-linked,

![Figure 2. (a) Storage modulus and (b) loss modulus of PA6/PDA1 blends. (c) Storage modulus and (d) loss modulus of PA6/EDA3 blends.](https://example.com/figure2.png)
it is infusable in the melt so that the solid content contribution to the viscosity is insignificant according to the Einstein equation.\textsuperscript{41} Furthermore, if it is due to the cross-linked structure, the rheological properties should continue to increase as the amount of diamine (PDA1 or EDA3) increases. However, after the optimum ratio of 0.1 for both diamines, at which the rheological properties reached their peaks, they were reduced, indicating that they cannot be reconciled with cross-linking reactions as there will definitely be more cross-linking reactions with more linking agents to enhance those properties.\textsuperscript{1,3,33,34}

For the correct interpretation of the rheological behavior, the occurrence of topological structure change is more feasible. The appearance of branching structure is the most likely since the melt viscosity of a branched polymer grows exponentially with the molar mass of the arm \((\eta_0 \approx (M_c/M_s)^{3/2} \exp(\nu M_c/M_s))\), where \(M_c\) is the arm’s molecular weight, \(M_s\) is the entanglement molecular weight, and \(\nu\) is the constant that is independent of the number of arms, \(f\) (3 or 4 gave the same results).\textsuperscript{39,42} In our previous report, the viscosity of the modified PA6 reached \(1 \times 10^5\) Pa·s because the commercial PA6 molecules whose weight average molar mass was \(8.5 \times 10^4\) g/mol with a polydispersity index of 3.5 reacted to form the modified PA6.\textsuperscript{13} Since the amount of linking agents in PA6/diepoxide reactive mixtures was quite small compared to polymer molecules, it is very likely that a branched structure was formed instead of the cross-linking structure.\textsuperscript{7,42} The growing caprolactam anion can attack the amine group of diamines (Schemes 2 and 3). The connection of two growing PA6 molecules into one through the diamine can increase the molar mass, which can lead to more chain entanglements and higher viscosity due to slow relaxation (Scheme 2). The anion attack can occur on the same amine group or on both amine groups of diamines. The first case induces another reaction on the other amine group to form three or four branched molecules (Scheme 3). However, a steric interference in the three-arm molecule can prevent the formation of the four-armed molecule. In our experiments, slightly branched PA6 was easily generated due to the relatively high temperature and shear rate polymerization conditions in the extruder and the use of a bifunctional activator. Branched polymers require greater strain to untangle the molecules and allow them to flow, resulting in a large increase in the storage modulus and loss modulus.\textsuperscript{39,42}

The DSC scanning result for heating of the PA6/diamine mixtures is listed in Table 1. Upon introduction of the diamine, both the enthalpy of melting \((\Delta H_m)\) and crystallinity \((X_c)\) were reduced, but the melting temperature did not show a notable change. It indicates that the crystallization of PA6 was hindered by the branching structure. Similar results have been already reported with different kinds of linear chain extenders.\textsuperscript{7,43,44} In those studies, the decrease in crystallinity was attributed to the increase in molecular weight, which hinders the arrangement of macromolecules in a crystalline phase. The decrease in crystallinity was largely affected by the increase in molecular weight and the hindrance by the chain branching. To investigate the crystalline structures, WAXD analysis was performed, and the results are shown in Figure 3 and Table 1. The WAXD spectra for PA6/EDA3 mixtures showed two sharp characteristic peaks at \(2\theta = 20^\circ\) and \(23^\circ\). Both peaks correspond to the reflection of the \(\gamma\)-crystalline planes \((200)\) and \((002) + (202)\), respectively.\textsuperscript{55} There are no other peaks observed in WAXD profiles such as the \(\gamma\)-crystalline peak, which exists at \(2\theta = 21.5^\circ\) corresponding to the \((001)\) plane.\textsuperscript{31} The crystallinity dropped from 43.1% for neat PA6 to 35.0–39.0% for diamine-added PA6. This indicates that the branched structure hindered the crystallization of PA6, consistent with the DSC results, but its structure was the same as the main chain of PA6. Therefore, the synthesized polymer can be recycled as normal PA6, which is helpful to reduce the environmental issue.

The mechanical properties of the PA6s with different molar ratios of diamines are shown in Figure 4. Both diamine-added PA6s show almost the same behavior. Until the molar ratio became 0.1, the tensile modulus and tensile strength increased with the addition of diamines due to the enhanced molecular weight. Generally, modulus and tensile strength of linear polymers are reduced as the crystallinity decreases. Despite the reduction of crystallinity, however, the modulus and tensile strength of all PA6s were improved with the addition of diamine since the molecular weight and the number of branched molecules were increased and more chain entanglements occurred.\textsuperscript{42,43} Chain entanglements increased with molecular weights and formed branches that lead to significant improvement in elongation at break. This is different from Steeman and Nijenhuis’s report.\textsuperscript{14} They measured the rheological and mechanical properties of a series of linear and randomly branched PA6 samples. The mechanical properties show minor differences between the linear and moderately branched samples. Although the yield stress and tensile modulus of the branched PA6 were \(10–15\%\) higher than those of linear PA6, there was a minor loss of yield strain. This can be due to the difference in the number of branches. Their PA6 can have more branches than the current study. The branching structure proposed in this study can affect the entanglements between chains. Thus, the energy absorbed to break (modulus of toughness or tensile toughness) was nearly tripled due to the improved ductility of the modified PA6 and the improved tensile modulus. After the mechanical properties of the modified PA6 reached the peaks, they were decreased as the amount of diamines exceeded the molar ratio of 0.1. However, for those PA6s including diamines with a molar ratio of more than 0.1, the mechanical properties of the blends were still superior to those of neat PA6, which is plausibly due to the formation of a branched structure. The more diamines added that exceeded the 0.1 molar ratio, the more quenching of the propagation reaction occurs, and the molecular weight becomes low to show reduced performance, although the modified PA6 is still better than the neat PA6.
CONCLUSIONS

In this study, we successfully polymerized PA6 with diamines by reactive extrusion from the ε-caprolactam monomer. Two different diamines were added, but the products showed nearly the same physical properties and similar molecular weights regardless of diamines, suggesting that their reactivity and the reaction mechanism were almost alike. In the extruder, ε-caprolactam completely reacted to form a PA6 polymer composite without any residual monomers. PA6 containing diamines showed a highly increased melt viscosity and stronger shear thinning effect than neat PA6 over the entire frequency range. It was induced by increased molecular weight and chain entanglements due to the chain branching. The storage modulus and loss modulus also showed more solid-like behavior and increased with the concentration of diamine. All rheological properties were increased until the molar ratio of diamines to initiator reached 0.1. After then, further addition of diamines showed deteriorated rheological properties due to the quenching effect of diamines. PA6 molecules possibly formed branched structures during the polymerization because of the added diamines, high polymerization temperature, high shear rate in the extruder, and the bifunctional activator. PA6 chains were connected and/or formed the branched structures, which led to an increase in molecular weight as well as more entanglements. Beyond the optimum amount of diamine concentrations (0.1 molar ratio of the initiator), the molecular weight decreased because of the quenching effect of diamines.

The mechanical properties of the diamines including PA6 were significantly improved with the diamine addition until the molar ratio reached 0.1. In particular, the elongation at break and the breaking stress were significantly increased. After the optimum amount, the mechanical properties decrease due to the reduced molecular weight and/or the reduction of branching structure but still better than those of linear PA6. The addition of diamines to produce randomly branched PA6 molecules enables us to obtain PA6 resins with superior rheological and mechanical properties that are unattainable for linear PA6 to open up new opportunities for wider applications. Produced PA6 has a merit of processibility in the extrusion process such as a blow molding process in which stability against sagging under gravity is required and other processes where elongational properties dominate. Also, the synthesized polymer has the same repeating units as PA6 to let them be recycled as normal PA6. This can be helpful to reduce the environmental issue.

EXPERIMENTAL SECTION

Materials. ε-Caprolactam used in this study was procured from Capro Corporation (Korea). Sodium hydride, terephthaloyl chloride, triethylamine, pyridine, resorcinol, p-phenylenediamine (PDA1), 4-nitrobenzoyl chloride, and activated Pd-carbon (10%) were purchased from Aldrich. TBC was synthesized by the reaction of terephthaloyl chloride with caprolactam in benzene.33 3-(4-Aminobenzoyloxy)phenyl 4-aminobenzoate (EDA3) was synthesized according to the method reported previously (see Figure 5 for chemical structures of TBS, PDA1, and EDA3).24

Synthesis of Sodium Caprolactam (Na-CL). ε-Caprolactam was dried for 24 h at 100 °C in a convection oven and vacuum-dried at 50 °C for 48 h to remove the moisture completely. First, 1 mol of dried ε-caprolactam was placed in the round flask under an argon atmosphere. After ε-caprolactam was completely melted at 70 °C, 0.05 mol of
sodium hydride was added with stirring. After the hydrogen emission was ceased, the mixture was stirred for 10 min under an argon atmosphere to complete the reaction. The mixture was cooled to room temperature and pulverized. Sodium caprolactam powder was stored in a container filled with argon.

In Situ Polymerization by Reactive Extrusion. The reactant mixture consisted of ε-caprolactam, sodium caprolactam, TBS, and diamines used as a monomer, an initiator, an activator, and additives, respectively. The monomer/initiator/activator molar ratio was optimized as 50:1:0.5 in preliminary experiments for both high polymer yields and short polymerization times. The molar ratio of diamine content to initiator varied as 0.05, 0.1, 0.15, and 0.2 for each sample. The reactant mixtures were fed into a twin screw extruder (BA-19, Bautech), while argon was flowing to prevent quenching of active anions due to moisture during polymerization. The temperature profile from the feeding zone to the die was set to 140/180/200/220/220/230/240 °C, and the screw speed was set to 50 rpm. The extruded diamine-containing PA6 was pelletized and dried at 60 °C under vacuum for sufficient time before characterization.

Characterization. Differential scanning calorimetry (DSC 823e, METTLER TOLEDO) was used to analyze the thermal properties of PA6/diamine compounds. Under a nitrogen atmosphere, the sample was first heated from 25 to 280 °C at 10 °C/min, cooled to 25 °C, and heated to 280 °C at the same heating rate. The degree of crystallinity (Xc) was calculated using the following equation.

\[ X_c(\%) = \frac{\Delta H_m}{\Delta H_{100}} \times 100 \]

where \( \Delta H_m \) is the specific enthalpy of melting, and \( \Delta H_{100} \) is the enthalpy of melting with 100% crystalline nylon 6 (190 J/g).\(^{25}\)

WAXD (D8 Advance, Bruker Miller Co.) was used to analyze the crystalline order of the produced PA6. Prior to measurement, pelletized PA6 particles were hot-pressed at 240 °C and cooled to room temperature to obtain a film. The spectra were recorded at 25 °C with a diffraction angle (2θ) of 5°–40° with CuKα radiation. The intrinsic viscosity [η] was measured, and the viscosity average molecular weight was calculated. The Ubbelhode viscometer was used to check the time for polymer solution to pass through the capillary with 90% formic acid solution at 25 °C. Using the Mark–Houwink equation, the molecular weight of PA6 resin was calculated as [η] = k[M]\(^a\). The Mark–Houwink constants were \( k = 22.6 \times 10^{-3} \) (mL/g) and \( a = 0.82 \) for nylon 6 at 25 °C in a 90% formic acid solution.\(^{26}\)

Rheological properties were studied using Advanced Rheometric Expansion System (ARES, Rheometric Scientific). Samples were prepared by injection molding at 240 °C in a mold of 25 mm diameter and 1 mm thickness. Dynamic moduli (storage modulus (G') and loss modulus (G'')) and complex viscosity were measured between parallel plates at 250 °C with an applied strain of 10% and angular frequency from 0.05 to 500 rad/s. The degree of cross-linking was determined using a solvent extraction method (ASTM D2765) by m-cresol for 20 h of reflux.\(^{27}\) A UV spectrometer (Agilent 8453 UV–Vis system) was used to analyze the chain regularities in PA6 chains. The presence of structural irregularities in PA6 chains can be absorbed in the UV region with the optical density maximum (OD\(_{max}\)) at 270–280 nm.\(^{28}\) PA6 solutions (1 wt %) in formic acid were prepared, and the UV absorption was measured between 250 and 400 nm (1 cm path length).

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