Miscibility and mechanical properties of aryl-aliphatic polyamides/nylon 6 molecular composites

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Summary

A series of aryl-aliphatic polyamides, copoly(4,4'-diaminobenzanilide-adipamide/2,6-naphthalamide)s, with feed mole ratios of adipic acid/2,6-naphthalene dicarboxylic acid of 1/9, 3/7, and 5/5 were synthesized. A new family of molecular composites based on the synthesized aryl-aliphatic polyamides and nylon 6 has been discovered. The molecular composites were found to have at least partial miscibility between aryl-aliphatic polyamides and nylon 6. Well-defined aryl-aliphatic polyamide microfibrils a few nanometers in diameter were observed in the molecular composites. 10 wt% aryl-aliphatic polyamide clearly promoted the toughness of nylon 6.

Introduction

Molecular composite is essentially a mixture of stiff and flexible coil macromolecules which is conceptually similar to a fiber-reinforced polymer except that reinforcement takes place at a microscopic level (1-6). This composite is expected to have a higher modulus and greater strength than a fiber-reinforced polymer because of the high aspect ratio of a rigid rod polymer molecule. Takayanagi and co-workers have reported on composites of more conventional polymers with the poly-p-phenylene terephthalamide (PPTA) reinforcing polymer (5,6). The rod-like polymer PPTA was found to be insoluble in common organic solvents such as m-cresol and N-methylpyrrolidone (NMP) but was soluble in the strongest acids such as sulfuric acid. Therefore, it is very dangerous and difficult to process PPTA into molecular composites.

We synthesized a series of copoly (4,4'-diaminobenzanilide-adipic acid/2,6-naphthalamide) with various feed mole ratios of adipic acid/2,6-naphthalene dicarboxylic acid. All the polymers were soluble in NMP containing LiCl because the following reasons. First, the use of 4,4'- diaminobenzanilide in the synthesis. 4,4'-diaminobenzanilide would maximize polymer solubility since the monomer is

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unsymmetrical (7). Second, referred to F. Laupretre (8), naphthalene segments are not chiefly responsible for the chain stiffness of aryl- aliphatic polyamide, so these groups can be replaced to a large extent by tetramethylene units having relatively high entropy without seriously destroying the rigidity of the polymers; therefore, polymer solubility is improved and still keeps the overall rod-like nature of the polymer chain. Also, the aryl-aliphatic polyamide containing tetramethylene groups may be able to enhance the miscibility of molecular composites. This study is first to prepare aryl-aliphatic polyamides/nylon 6 /NMP containing LiCl ternary solutions. The molecular composites were prepared precipitating the ternary solutions into deionized water.

The characteristics of molecular composites were examined by means of a differential scanning calorimeter (DSC), dynamic mechanical analyzer (DMA), scanning electron microscope (SEM), and transmission electron microscope (TEM), The mechanical properties were investigated using a tensile tester.

Experimental

Synthesis

We used modified Higashi phosphorylation reaction (9) to yield a series of aryl-aliphatic polyamides. The following monomers were used without further purification: 2,6-naphthalene dicarboxylic acid (TCI), adipic acid (Merck) and 4,4'-diaminobenzanilide (TCI). In a typical polymerization, 8 mmole diacid and 8 mmole diamine were dissolved in a mixing solvent consisting of 50 ml of NMP containing 3 grams $CaCl_2$, 0.57 grams LiCl, 6.5 ml pyridine, and 16 mmole of triphenyl phosphite. The reaction continued for 2 hours at 120°C under nitrogen. The polymer composition was estimated by Proton NMR spectroscopy. According to the feed mole ratios of adipic acid/2,6-naphthalene dicarboxylic acid, 1/9, 3/7, and 5/5, respectively, the corresponding polymers were denoted as PA(10), PA(30), and PA(50).

Preparation of molecular composites

The nylon 6 used in this study was produced under the trade name Capron 8200 by Allied-Signal Inc.; its inherent viscosity was 1.68 dl/g in sulfuric acid. The aryl-aliphatic polyamides and nylon 6 were dissolved separately in NMP containing 2 wt% LiCl at room temperature and 70°C, respectively. The polymer concentration was about 1 wt%. These solutions were further mixed in various proportions by stirring with a magnetic stirrer for about 1 day. The clear ternary solutions were precipitated by dropwise addition into an excess of vigorously stirred deionized water. The precipitate were washed exhaustively in methanol, filtered and dried in a vacuum oven at 80°C for 24 hours to yield a precipitated blend in the form of a flake. For measurement of mechanical properties, the blend flakes were compression molded into thin films approximately 0.1-0.3 mm in thickness, and the nylon 6 was subjected to a preparation route identical to that used for their blends in order to provide a uniform point of reference. Thin film samples for tensile testing of aryl-aliphatic polyamides were cast from a 1.5 wt% solution of polymer in the NMP containing 1 wt% LiCl solvent, and dried at 80°C in a dust-free chamber until tack-free; then, films were dried in a vacuum at 80°C for 24 hours and immersed in 80°C water for 3 days to remove any residual solvent and salt. The LiCl content of the films could not be detected by using an Inductively-Coupled Plasma Atomic Emission Spectroscope. This suggested that LiCl was removed completely after washing. These films were approximately 0.05-0.1 mm in thickness. To exclude moisture, the samples were stored over anhydrous calcium chloride until used.
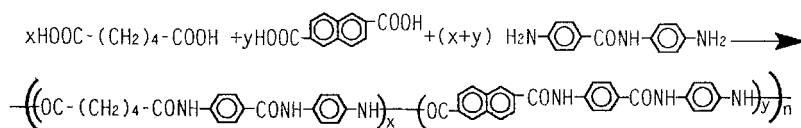
Measurements

Proton NMR spectra were obtained on a JEOL EX400 at 400 MHz in deuterated sulfuric acid solution. Inherent viscosity(η_{inh})was measured at 0.1g/100ml in 96% sulfuric acid at 30°C. Thermal analysis were performed on a Du Pont 910 differential scanning calorimeter with a heating rate of 10°C/min. The loss tangent data (tan δ) of the samples were measured using a DMA 983 dynamic mechanical analyzer with a heating rate of 5°C/min and using a resonance frequency mode. Tg was determined as the maximum peak temperature of the loss tangent. By utilization of a Tensilon testing machine, the stress-strain behavior of the samples was investigated at a constant strain rate of 2%/min. The morphologies of the specimens were examined by using a scanning electron microscope (Hitachi S-800) and transmission electron microscope (JEOL JEM-1200EX II).

Results and Discussion

Aryl-aliphatic polyamides

Three kinds of aryl-aliphatic polyamides, each of which contained various feed mole ratios of adipic acid/2,6-naphthalene dicarboxylic acid, were synthesized by using a one-step procedure with the modified Higashi reaction. Thus, in all the reactions, adipic acid, 2,6-naphthalene dicarboxylic acid, and 4,4'-diaminobenzanilide, were reacted together, which reactions in turn were converted to random copoly(4,4'-diaminobenzanilide-adipic acid/2,6-naphthalamide) (scheme 1).

xHOOC-(CH₂)₄-COOH +yHOOC-⬡⬡-COOH+(x+y) H₂N-⬡-CONH-⬡-NH₂ ⟶

-{(OC-(CH₂)₄-CONH-⬡-CONH-⬡-NH)ₓ-(OC-⬡⬡-CONH-⬡-CONH-⬡-NH)ᵧ}ₙ

scheme 1

Table 1 summarizes the properties of the aryl-aliphatic polyamides showing that these aryl-aliphatic polyamides had good thermal and tensile mechanical properties. As expected, with increasing tetramethylene content, the Tg, modulus, and tensile strength decreased while the elongation at break increased.

DSC studies

Figure 1 shows the melting temperature (Tm) of the aryl-aliphatic polyamide/nylon 6 molecular composites for various compositions. All the composition ratios referred to subsequently in this study are on a weight basis. The depression of the Tm was an indication of strong interaction between the aryl-aliphatic polyamides and nylon 6. From Figure 1, it can also be observed that as the tetramethylene content increased in the aryl-aliphatic polyamides, Tm depression is also greater. This could reflect that increasing tetramethylene content in the aryl-aliphatic polyamide improved the miscibility of the studied molecular composites.

DMA studies

The variation of the tan δ as a function of temperature is shown in Figure 2 for the hot pressed films of the studied molecular composites. A maximum in tan δ was taken

Table 1. Summary of the properties of aryl-aliphatic polyamides.

Polymer	Composition x/y	η_{inh} (dl/g)	Tg (°C)	Tensile Strength (MPa)	Elongation at Break (%)	Modulus (GPa)
PA(10)	1/9	5.80	298	140	14	6.4
PA(30)	3/7	4.89	275	90	15	4.0
PA(50)	5/5	3.27	264	65	20	3.0
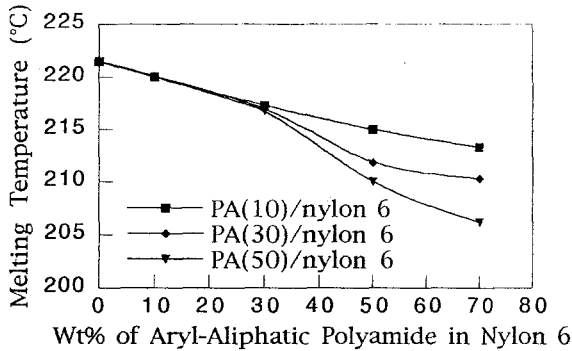
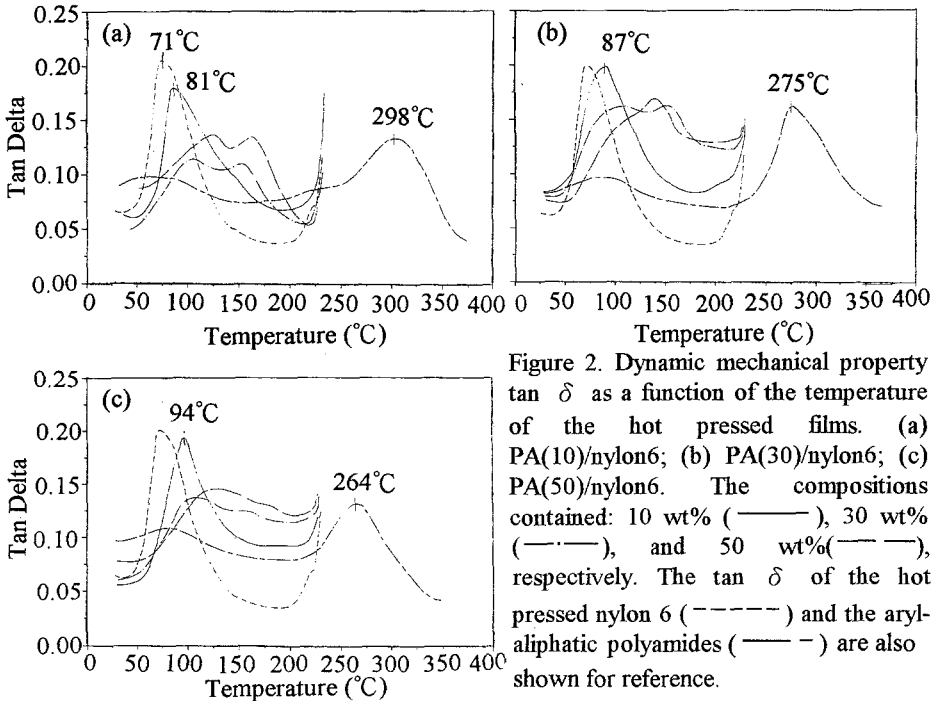Figure 1. The variation of the melting temperature with composition for aryl-aliphatic polyamide/nylon 6.

Figure 2. Dynamic mechanical property tan δ as a function of the temperature of the hot pressed films. (a) PA(10)/nylon6; (b) PA(30)/nylon6; (c) PA(50)/nylon6. The compositions contained: 10 wt% (————), 30 wt% (—·—), and 50 wt%(———), respectively. The tan δ of the hot pressed nylon 6 (—————) and the aryl-aliphatic polyamides (———) are also shown for reference.

as a measure of Tg. The Tg of PA(10), PA(30), and PA(50) was 298°C, 275°C, and 264 °C, respectively. With the addition of 10 wt% of aryl-aliphatic polyamide to nylon 6, the tan δ peak of all molecular composites shown a single tan δ peak, and the peak temperatures of these molecular composites shifted to higher temperatures than did that of nylon 6. Considering the temperature of the tan δ peak, the peak temperature increased in the order PA(50)/nylon 6, PA(30)/nylon 6, and PA(10)/nylon 6, corresponding to the values of the tan δ peak at 94°C, 87°C, and 81°C, respectively. This trend was opposite to that of the PA(10), PA(30), and PA(50) aryl-aliphatic polyamides. This suggested that the order of compatibility of these molecular composites was as follows: PA(50)/nylon 6 (1/9) > PA(30)/nylon 6 (1/9) > PA(10)/nylon 6(1/9). For 30 and 50 wt% aryl-aliphatic polyamide content, it was found that all the specimens were partially miscible with two tan δ peaks shifting inwards. In contrast, the loss tangent data of the as-precipitated flakes of nylon 6 blended with 30 wt% of different aryl-aliphatic polyamides indicated a broaden single peak, suggesting that these composites have better miscibility. Consequently, the rapidly coagulating process could obtain more miscible molecular composite systems, and thermal-induced phase separation was a general phenomenon in these studied molecular composites.

Morphology

In general, aryl-aliphatic polyamide is considered to be an essentially semi-rigid polymer; thus, the unfavorable thermodynamics of mixing with flexible nylon 6 may lead to phase separation of the molecular composites. Figure 3(a) is the liquid nitrogen frozen fractured surface of PA(50)/nylon 6 (3/7) casting film. Preparation of the casting film followed the procedure for the aryl-aliphatic polyamide film. It shows a porous structure, suggesting serious phase separation. Nevertheless, we overcame this problem of serious phase separation kinetically by rapidly coagulating the ternary solution in non-solvent to obtain molecular composites. The same composition of PA(50)/nylon 6 (3/7) hot pressed film showed a dense morphology (Figure 3(b)).

Figure 4 shows the scanning electron micrographs of the hot pressed films of the molecular composites containing 30 wt% aryl-aliphatic polyamide. All the specimens were etched with 99% formic acid for 10 days. Nylon 6 could not be thoroughly dissolved from composite using this etching method. This result implies that a strong specific attractive interaction exists between the aryl-aliphatic polyamide and nylon 6. The residual of specimen showed a microfibrils shape with a diameter of a few nanometers. The etched surfaces of the aryl-aliphatic polyamides/nylon 6 (1/9) composite films reveal thinner microfibrils than were found in the aryl-aliphatic polyamides/nylon 6 (3/7) composite films. It suggested that the aryl-aliphatic polyamide molecules with lower aryl-aliphatic polyamide content formed a thinner microfibril than that with higher aryl-aliphatic polyamide content. This also indicates that an increase of aryl-aliphatic polyamide content induced more obvious phase separation of the aryl-aliphatic polyamide from the nylon 6. To clarify the dispersed state of the aryl-aliphatic polyamide in the aryl-aliphatic polyamides/nylon 6 (3/7) hot pressed films, the nylon 6 was extracted with 99% formic acid, and the remaining aryl-aliphatic polyamides were surveyed with a transmission electron microscope. Figure 5 shows that all aryl-aliphatic polyamides studied here had microfibrillar networks. The diameters of microfibrils were very small, ranging from 5 nm to 15 nm.

Mechanical properties

The mechanical properties of the molecular composites were evaluated from the
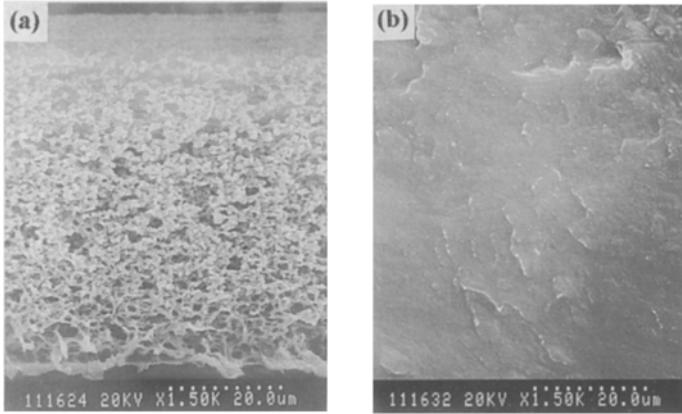
Figure 3. Scanning electron micrographs of the liquid nitrogen frozen fractured surfaces of (a) PA(50)/nylon 6 (3/7) casting film and (b) PA(50)/nylon 6 (3/7) hot pressed film.
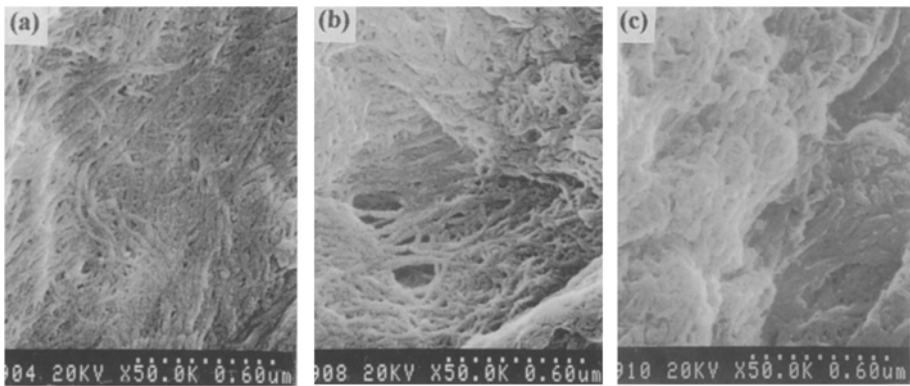

Figure 4. Scanning electron micrographs of the etched surfaces of hot pressed films. (a) PA(10)/nylon (3/7); (b) PA(30)/nylon 6 (3/7); (c) PA(50)/nylon (3/7).
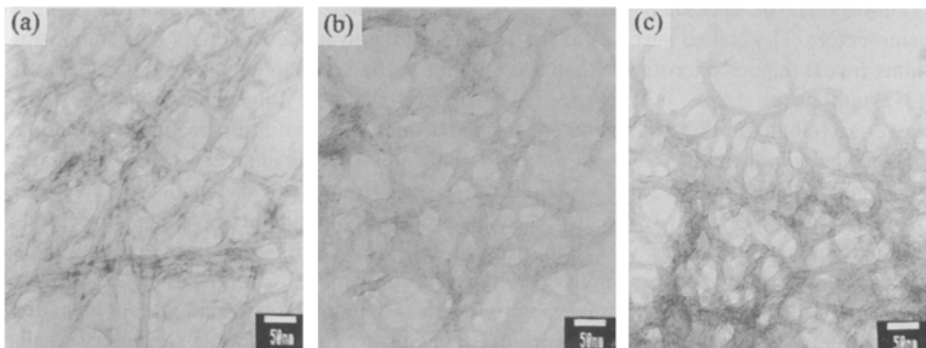

Figure 5. Transmission electron micrographs of microfibrillar networks of (a) PA(10),(b) PA(30), and (c) PA(50), which remain after extraction of nylon 6 with formic acid from the molecular composites.

stress-strain curves. Figure 6 gives a typical example of the stress-strain curves of the PA(10)/nylon 6 composites containing 10, 30, and 50 wt% aryl-aliphatic polyamide compared to the curve for nylon 6. All the specimens were heat-compressed at 230℃ for 5 min. The values of the mechanical properties are given in Table 2. As expected, the young's modulus of the molecular composites increased with increasing aryl-aliphatic polyamide content. The increase in tensile strength in the blends containing 10 wt% aryl-aliphatic polyamide were more significant, because the aryl-aliphatic polyamide had excellent compatibility with the nylon 6 matrix. In the PA(10)/nylon 6 molecular composite, no apparent reinforcing effect was realized when the PA(10) content was 30 and 50 wt%. This result may be due to the following reasons: (1) From DMA studies, the material had obvious phase separation, revealing that the compatibility of PA(10) with nylon 6 is poor. The poor compatibility usually results in poor tensile mechanical properties. (2) The higher melt viscosity of the materials resulted in difficult flow at hot-compression. The voids and cracks occurred as a result of the manufacturing process. Because voids and cracks are stress concentration centers, the material fails prematurely during loading. SEM micrograph of the liquid nitrogen frozen fractured surface PA(10)/nylon 6 (3/7) is shown in Figure 7. A rough and heterogeneous appearance with a few voids was observed for the PA(10)/nylon 6(3/7). In contrast, the PA(50)/nylon 6(3/7) (figure 3(b)), a dense fractured surface with a homogeneous image was observed. It is concluded, therefore, that the low tensile strength in the PA(10)/nylon 6 system containing higher PA(10) was mainly attributable to the poor compatibility of PA(10) and nylon 6 and the presence of a few voids.

When the molecular composites contained more than 30 wt% aryl-aliphatic polyamide, the ductility almost disappeared, and a stiff and brittle nature was conspicuous. The explanation for this result is that aryl-aliphatic polyamide formed a more perfect and stronger microfibril in nylon 6 and the materials contained a few voids. This is evidenced by the SEM and TEM micrographs shown in Figures 4, 5 and 7, respectively. The rigid microfibril restrained the ductile deformation of the nylon 6 giving low ultimate elongation.

The interesting observation in this study is the high elongation at break without sacrifice of strength and modulus for the molecular composites containing 10 wt% aryl-aliphatic polyamide. The increase of ductility may have been due to several reasons. First, it is a decrease of the overall crystallinity of the blend. The heat of the fusion of the hot pressed aryl-aliphatic polyamide/nylon 6 (1/9) composites was about 90% of that of the hot pressed nylon 6. This was found by DSC measurement. Second, it is thought to be because the aryl-aliphatic polyamide had better compatibility with nylon 6 and hence slow crack growth due to dissipating energy in the plastic deformation. The tensile fractured surface of nylon 6 showed a zone with rapid crack propagation, whereas that phenomenon was not found in the molecular composites containing 10 wt% aryl-aliphatic polyamide. Third, an intense stress-whitening phenomenon was observed on the tensile fractured specimens. Bucknell and Smith (10) remarked on the connection between crazing and stress-whitening. They concluded that the difference between stress-whitening and crazing exists merely in the size and concentration of the craze bands, these being of larger size and greater quantity in stress-whitening. Thus, the higher conversion of the materials into crazes accounts for the high breaking elongation of molecular composites containing 10 wt% aryl-aliphatic polyamide. The overall morphology facilitates the formation of crazes as well as their termination, so that the materials are able to sustain larger plastic deformation prior to fracture.
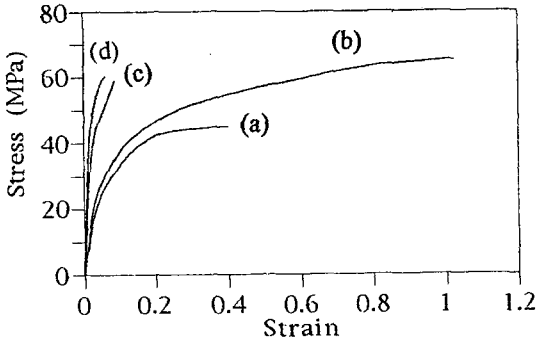
Figure 6. Stress-strain curves of the hot pressed films of (a) nylon 6, (b) PA(10)/nylon 6 (1/9), (c) PA(10)/nylon 6 (3/7), and (d) PA(10)/nylon 6 (5/5).
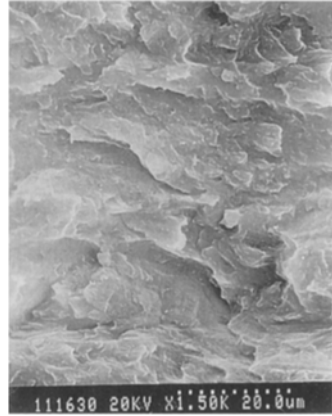

Figure 7. Scanning electron micrograph of the surface of PA(10)/nylon 6 (3/7) hot pressed film fractured in liquid nitrogen.

Table 2. Mechanical properties of nylon 6 and molecular composites.

Sample	Tensile Strength (MPa)	Elongation at Break (%)	Modulus (GPa)
Nylon 6	45	40	0.7
PA(10)/nylon 6(1/9)	65	102	0.9
PA(10)/nylon 6(3/7)	60	9	2.0
PA(10)/nylon 6(5/5)	61	6	2.9
PA(30)/nylon 6(1/9)	59	136	0.8
PA(30)/nylon 6(3/7)	70	10	1.9
PA(30)/nylon 6(5/5)	85	6	3.0
PA(50)/nylon 6(1/9)	63	170	0.8
PA(50)/nylon 6(3/7)	71	20	2.1
PA(50)/nylon 6(5/5)	80	6	2.8

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