

Development of New Functional Materials Based on Polyamides

*Shuichi Maeda**

Polymer Research Laboratory, UBE Industries, Ltd.,
1978-96, Kogushi, Ube, Yamaguchi 755-8633, Japan
27460u@ube-ind.co.jp

Introduction

Polyamides like nylon6 and nylon66 have already been produced industrially in the 1930s. At the first throw-off, polyamides were mainly developed for the application of fiber and textiles. Since 1950s, polyamides have been developed for the injection molded materials on account of their excellent properties and become one of the most popular engineering plastics.

Polyamides have been widely used in the various industrial fields. Especially the largest market with more than 40% of the total demand is in automobiles and transportation equipment. In this lecture, we would like to introduce several new functional materials based on polyamides developed by UBE.

New Polyamide Elastomer "UBESTA XPA"

UBESTA is the trademark for UBE's polyamide12. UBESTA XPA is a novel, superbly balanced polyamide elastomer (PAE) developed by UBE's specific technology. UBESTA XPA shown in Figure 1 is a novel multi-blocked polyetheramide, composed of polyamide12 as hard segments and new polyether as soft segments.

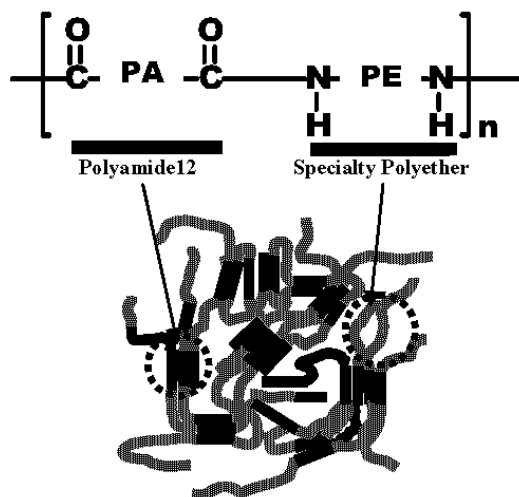


Figure 1. Chemical structure and schematic representation of micro phase separated structure for UBESTA XPA.

UBESTA XPA has three grades with different shore hardness. XPA9063 is the hardest grade with D63, XPA9055 is medium one with D55 and XPA9044 is the softest one with D44. Figure 2 shows AFM images of the surface of injection molding of XPA9044. In this

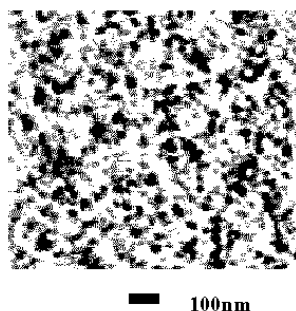


Figure 2. Tapping mode AFM phase images for a surface of injection molding of XPA9044.

figure bright and dark colors represent parts having high and low modulus, respectively. It is clearly shown that a micro phase separated structure in XPA is formed with dozens of nanometer scale.

Figure 3 shows that cycle times to form the crack in specimens on flexural fatigue test (DeMattia test) at 296, 253 and 233K for UBESTA XPA and other PAE. As can be seen from this figure, the flexural fatigue resistance of UBESTA XPA is better than that of other PAE over wide temperature range. It is supposed that the excellent flexural fatigue properties for UBESTA XPA are attributed to the completely amorphous state of soft segment having low T_g due to its molecular structure and the good miscibility between hard and soft segment.

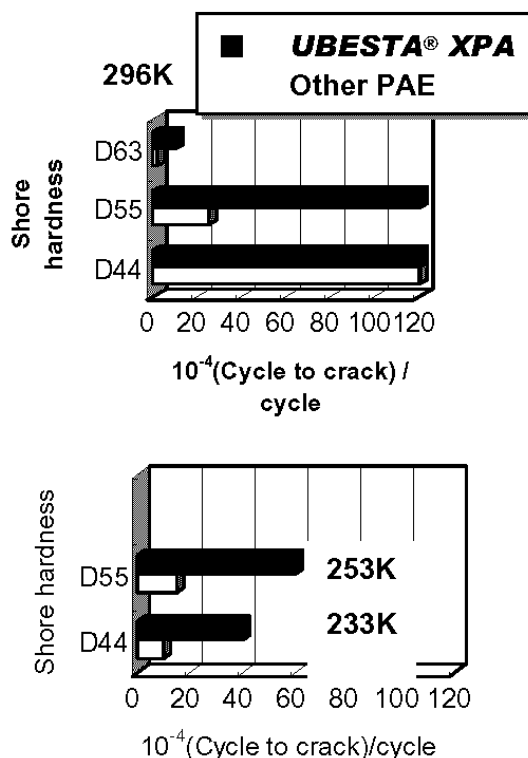


Figure 3. Relation between cycle times to form the crack on flexural fatigue test at 296, 253 and 233K and shore hardness for UBESTA XPA and other PAE.

In addition to the properties mentioned above, UBESTA XPA has many significant features in elasticity, flexibility, transparency, gloss, low density, hydrolytic stability, adhesion with thermoplastic polyurethanes, etc. One of the examples adopted recently as shoe sole material is shown in Figure 4. The key points for adopting UBESTA XPA are fatigue properties, adhesive properties, elasticity and transparency.



Figure 4. An example adopted as a shoe sole material.

UBESTA Gas Pipe System

We have developed the gas pipe system using UBESTA which is superior in gas barrier and mechanical properties to polyolefins. UBESTA gas pipe system has a good track record of over 22,500 km in gas pipe and joint system for natural gas in Australia. To achieve higher reliability and easier installation of the gas pipe system, we have developed a new joining system using a laser beam. This laser fusion joining system is superior in joint strength, welding activity, cost, etc.

We have also developed branched nylon12 to improve the mechanical and rheological properties of UBESTA. Imino-dodecanoic acid (IDA) is used for syntheses of branched polyamide12 as branching agent[1]. In Figure 5, the intrinsic viscosities are plotted against the weight-average molecular weight (M_w) for samples used in this study. The straight line in this figure represents an equation shown by Hammel et al. for linear polyamide12 in 1,1,1,3,3,3-hexafluoro-2-propanol solution and has the slope of 0.68[2]. Figure 5 shows that Hammel's equation agrees fairly well with the values of both L12 series (linear polyamide12) and LP (a commercial grade), while the values of B12 series (branched polyamide12) are slightly lower than those calculated from Hammel's equation. Compared at the same value of M_w , the ratio of intrinsic viscosities of B12 series to that of L12 series and LP is about 0.9. This represents that the branching structure is introduced to B12 series by polymerization with IDA that is trifunctional monomer. According to Zimm and Kilb theory[3], the number of branching per a molecule for B12 series is found to be about one from the calculation. It is expected that B12 series are 3 arms star shaped polymers.

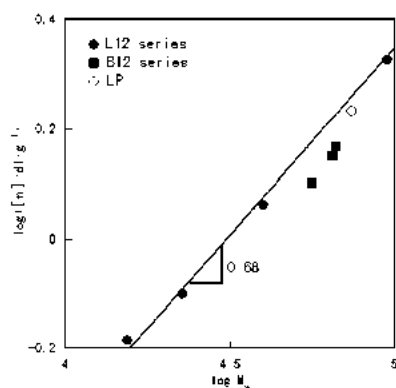


Figure 5. Intrinsic viscosities logarithmically plotted against weight-average molecular weights for polyamide12. Closed circles, closed squares and open circle indicate L12 series, B12 series and LP, respectively.

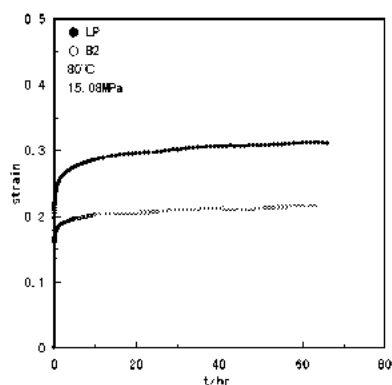


Figure 6. Creep behaviors at 353K plotted against time at constant stress (15.08MPa) for LP and B2.

In Figure 6, the creep behaviors at 353K are plotted against time at constant stress (15.08MPa) for LP and B2. The sample code B2 is a prototyped sample. The degree of crystallinity of LP sample evaluated from specific gravity is about the same as that of B2. Though the M_w

(74.0k) of LP is higher than that (64.6k) of B2, creep strain for LP at long time region is larger than that for B2. We consider that the branched chain sections between lamellas are difficult to relax and stretch at high load creep test.

New Polyamide Terpolymer "TERPALEX"

TERPALEX has been developed as a new special copolymer which is composed of three monomer polyamide6, polyamide66 and polyamide12. This material is used as the thermoforming film in the package field instead of copolyamide6/66 (PA6/66) and copolyamide6/12 (PA6/12). As a result of ternary copolymerization, TERPALEX is supposed to restrain intermolecular interaction through hydrogen bonding. This novel terpolymer TERPALEX combines the good usage properties such as higher shrinkage property, deeper thermoforming capability, lower melting point, higher transparency and better flexural resistance. The basic properties of TERPALEX are tabulated in Table 1 in comparison with PA6/66 and PA6/12 having same polyamide6 content.

Table 1 Properties of TERPALEX, PA6/66 and PA6/12

	Unit	Method	TERPALEX	PA6/66	PA6/12
T_m	K	UBE	463	469	472
T_c	K	UBE	407	423	415
Tensile strength ^{*1}	MPa	ASTM D882	100	105	95
Tensile modulus ^{*1}	MPa	ASTM D882	560	600	700
Flex crack resistance ^{*1}	Holes /0.04m ²	MIL B-131C	<15	<15	<20
	273K/200cycles				
Haze ^{*2}	%	ASTM D1003	9	14	8
Flex crack resistance ^{*2}	Holes /0.04m ²	MIL B-131C	5	8	5
	273K/200cycles				
Depth ^{*3} at thermoforming test	mm	UBE	30	24	25

^{*1} T-die casted monolayer film with a thickness of 30 micrometers.

^{*2} 5-layer film composed of PA/ad/LDPE/ad/LLDPE.

^{*3} T-die casted monolayer film with a thickness of 100 micrometers. Deep-drawing condition; 353K and 20 mmHg.

Conclusions

We believe that "UBESTA XPA, UBESTA Gas Pipe System and TERPALEX" will be the key to success for the value-added product development.

References

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