Fracture and Impact Properties of Modified Nylon 11

QI FANG LI, MING TIAN, DONG GIL KIM, DE ZHEN WU, RI GUANG JIN

Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

ABSTRACT: Supertough nylon 11 is prepared by using a plasticizer. The influence of plasticizers on the impact property and tensile properties of plasticized nylon 11 were investigated. The results show that the impact strength is improved remarkably by methylbenzene sulfonamide, and the tensile strength is almost the same as that of natural-grade nylon 11. The study of the fracture morphology on plasticized supertough nylon 11 indicates that the fracture surface of plasticized supertough nylon 11 has a special feature, which is different from the fracture surface of general ductile polymer materials. It is similar to that of a multilayer distorted lamellar structure. There are many oriented fibrillar clusters on each layer, which are perpendicular to the impact direction. This was a new breaking phenomenon, which is found on supertough nylon 11. In regard to the experimental results, a "multilayer crack extension" mechanism is put forward. The fracture of supertough nylon 6 also verified this mechanism. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1600–1607, 2002

Key words: nylon 11; plasticizer; impact property; fracture mechanism

INTRODUCTION

Homopolymers can be roughly classified into pseudoductile and brittle polymers. Brittle polymers, such as polystyrene, styrene–acrylonitrile, and poly(methyl methacrylate), tend to fail with a crazing crack at a relatively low crack initiation and propagation energy. Pseudoductile polymers tend to shear yield with a relatively higher crack initiation energy, but with a low crack propagation energy. These polymers are brittle only under conditions of a sharp notch, plane strain, and high rates of deformation. Polymers classified in this category are nylon, PC, PVC, and POM, etc. The toughness of polymers can be improved by the dispersion of rubber particles[1,2] and the toughening mechanism of these systems can be explained by plastic deformation, such as crazing and shear yielding of the polymer matrix around these rubber particles. The matrix yield is the main mechanism of energy dissipation in pseudoductile polymer/rubber blends. The improvement of the impact strength often requires the incorporation of a rubber phase,[3,4] and the chemical structure of the incorporated rubbers has a significant effect on their dispersion in the matrix. Their viscosities at the extrusion temperature, the extrusion conditions, and extrusion machine performance all influence the impact strength of the resultant product.[5–8]

Up to now, various theories have been proposed to explain the toughening mechanism of rubber-blended polymers, including energy absorption by rubber particles, stress relief by cavitations around rubber particles, crack branching induced by rubber particles, crack termination at rubber particles, matrix crazing, shear yielding, combined crazing and yielding, toughened by a

Table I   Characteristics of Nylon 11 Resins Synthesized by the Beijing Academy of Chemical Engineering

Items	Properties
T_g (°C, DSC)	44
T_m (°C, DSC)	193
ΔH_f (J/kg)	2.26×10^5
Tensile strength (MPa)	58
Elongation (%)	65
Izod impact strength (J/m)	80
Density (g/cm^3)	1.05
Percentage of nitrogen (%)	7.6
Water absorption (%) (20°C, water)	1.8
HDT (1.82 MPa) °C	55

Table II   Characteristics of the Plasticizers

Designation	P1	P2
Mp (°C)	135–138	69
M_w	171.21	194.22
SO_4^{2-} (%)	0.02	—

nonelastomer, and Wu's percolation model.[9–15] These theories are derived from rubber-toughened polymers.

Recently, supertough nylon has been extensively researched in the polymer-modification field. In the nylon family, much toughening research on nylon 6 and nylon 66 have been reported,[16–24] but the literature on toughening nylon 11 is relatively sparse.[25,26] Nylon 11 is quite different from nylon 6 and nylon 66. Although all nylons have common characteristics, nylon 11 is superior to nylon 6 and nylon 66 in many properties. In this study, proper plasticizers dependent on the chemical structure of nylon 11 were selected to improve the impact properties of nylon 11. A supertoughened nylon 11 blend was obtained successfully. The toughening mechanism and fracture behavior of nylon 11 with the content of the plasticizer and different plasticizers, respectively, was investigated systematically. The fracture morphology of modified nylon 11 shows that the fracture behavior of such materials is different from that of other polymers. The pertinent mechanism is put forward in this article.

EXPERIMENTAL

A natural-grade nylon 11 sample was synthesized by the Beijing Academy of Chemical Engineering. Its characteristics are listed in Table I.

p-Methylbenzene sulfonamide ($CH_3C_6H_4SO_2$-NH_2)(P1) and *p*-butyl hydroxybenzoate (HO—C_6H_4—$COOC_4H_7$) (P2) manufactured by the Tian Jin Chemical Co. (Tianjin City, China) were employed. Their characteristics are listed in Table II.

Nylon 11 blends were obtained by a twin-screw extruder (L/D = 30, 30-mm diameter) at 220°C and 120 rpm. Extruded blends were molded into Izod bars (ASTM-D256, $\frac{1}{8}$ in. thick) and tensile bars (ASTM-D638) using an injection-molding machine with the mold temperature set at 220°C. Izod specimens were machined with a notch cutter. All samples were dried in a vacuum oven at 80°C for at least 12 h to ensure that they were completely dry before each melt-processing operation. The notched Izod impact strength of a dry-molded sample was measured at room temperature. The fracture surface was investigated by SEM using a Model S-250MK3 SEM from Cambridge. Tensile tests were carried out according to ASTM D638 with a crosshead speed of 10 mm/min on an Instron Model 4201.

RESULTS AND DISCUSSION

Tensile Properties

The tensile properties of nylon 11 blended with two plasticizers are summarized in Table III. The overall results clearly show that the yield strength decreases with the content of the plasti-

Table III   Tensile Properties of Plasticized Nylon 11 (Nylon 11 % + Plasticizer % = 100 wt %)

Sample	Yield Strength (MPa)	Tensile Strength (Mpa)	Elongation (%)	Modulus (MPa)
P1 = 0%	53.1	51.6	65.9	512
P1 = 3%	51	52	80	480
P1 = 5%	24.3	52.1	251	491
P1 = 10%	18.4	51.8	395	496
P1 = 15%	23.8	53.1	275	420
P1 = 25%	23.7	52.1	262	509
P2 = 10%	29.4	51.5	315	440
P2 = 15%	21.8	48.6	241	420
P2 = 25%	19.4	49.9	322	322
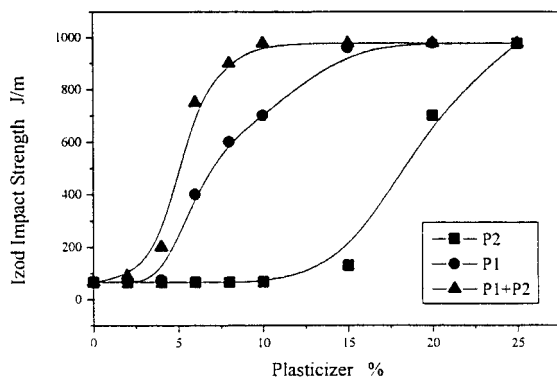
Figure 1 Izod impact strengths of nylon 11 blends with various contents of plasticizers at room temperature, where P1 : P2 = 1 : 1.

cizer, and the elongation increases significantly. It is unexpected that the tensile strength and tensile modulus are not dramatically decreased with the addition of the plasticizers.

It is generally known that a plasticizer enhances the molecular flexibility of polymers. The molecular chains of nylon 11 are easily oriented at the beginning of the tensile-strain process, and that results in retaining a high modulus of nylon 11, not like for the other polymers. Due to the breakdown of the hydrogen bond between the molecular chains of nylon 11 by adding a plasticizer, these well-ordered arrangements of molecular chains were destroyed with a further strain at the low deformation stage, and its interrelated yield strength clearly declined.

After yielding, the flexible molecular chains of nylon 11 are stretched at the high deformation stage, and entanglements of the molecular chains slipped. The tensile strength depends on the intermolecular interactions and the chemical bond of nylon 11; thus, the tensile strength does not decrease sharply with the content of the plasticizers. Indeed, the tensile strength of nylon 11 blended with the P1 plasticizer is slightly higher than that of nature-grade nylon 11.

Impact Strength of Plasticized Nylon 11

The Izod impact strength of pure nylon 11 is almost the same as that of pure nylon 6. On adding the plasticizer, its Izod impact strength increases dramatically and the Izod impact strength is 10 times higher than that of pure nylon 11. Figure 1 clearly demonstrates the effect of the plasticizer presence on the impact strength of nylon 11.

The low contents of plasticizers can efficiently increase the impact strength of nylon 11. Figure 1 also illustrates that there is an obvious ductile–brittle transition phenomenon with the plasticizer content, and the plasticizer contents which generate a ductile–brittle transition phenomenon, vary with the different plasticizers. The ductile–brittle transition of the nylon 11/P1 blend is generated within the range of 4–6% P1 content, while the ductile–brittle transition of the nylon 11/P2 blend is generated in the vicinity of 15% P2 content. The amount of plasticizers is determined by the plasticizing efficiency.

The amine (—NH$_2$) group of benzene sulfonamide can break the intermolecular hydrogen bond of nylon 11 more easily than can the OH group of butyl hydroxybenzoate, resulting in a high plasticizing efficiency. A mixture of P1 and P2 plasticizers shows a synergistic effect and has a better plasticizing efficiency, resulting in a lower ductile–brittle transition plasticizer content.
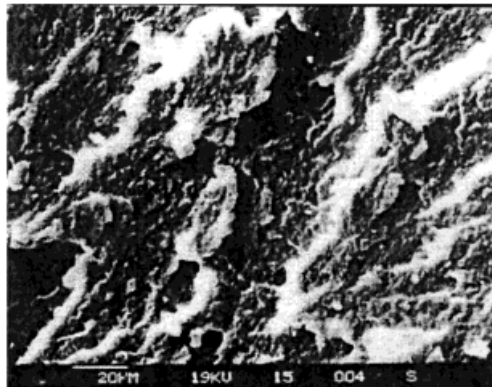
Fracture Morphology of Plasticized Nylon 11

The brittle fracture of pure nylon 11 shows a semicircle, centrosymmetrical, and radial fracture morphology (Fig. 2). A similar parabola-type or fin-type fracture morphology can often be observed in other materials. As the Poisson's ratio of microcrystals in nylon 11 is lower than that of the matrix, a large amount of the crazes will be initiated around the microcrystal, and the volume of the matrix will expand when it is impacted. The microcrystal in nylon 11 initiates stress concentration, which can result in a crack. As the mobility of molecular chains in nylon 11 is restricted due to the hydrogen bond, it becomes very weak and the free volume of the matrix is hard to expand. To cope with the swelling of the matrix resulting from the strain, the crazes quickly turn into cracks; at the same time, more stress-concentration points are initiated around the cracks, finally resulting in fracture of the materials.

There is either a similarity or difference between the ductile fracture and brittle fracture in plasticized nylon 11. The similarity depends on the multilayer microcracks initiated by the stress-concentration points resulting from microcrystals in the preliminary stage of fracture. The difference depends on the edges of the microcrack surfaces being connected to the opposite layer in the ductile fracture process rather than to microcracks developing into a large fracture surface.
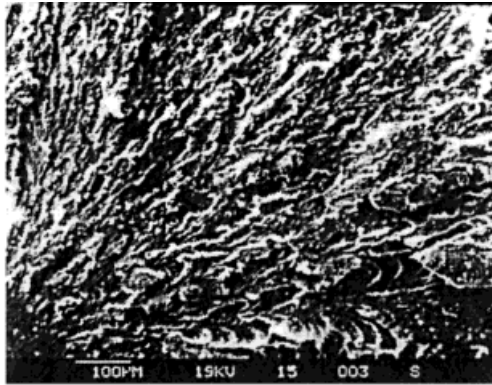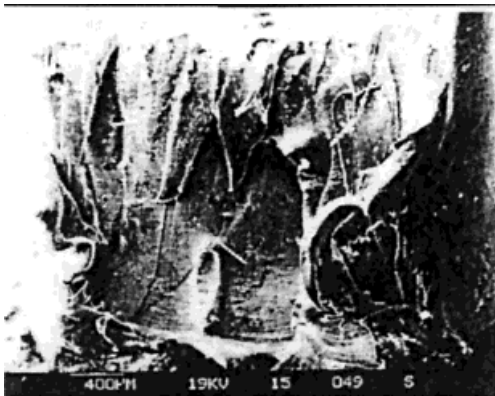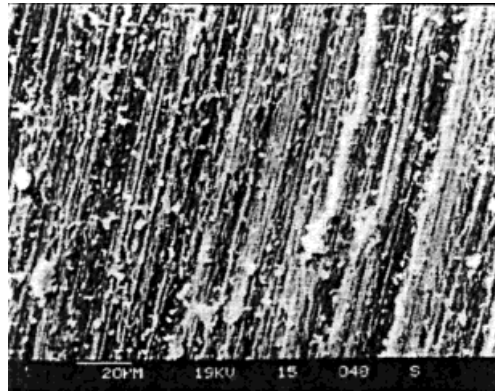
(a) magnifying multiple 80

(b) magnifying multiple 400

Figure 2   Fracture morphology of pure nylon 11.

The microcrack expands like a parabola, finally being split. The molecular chains in the layers are well-oriented, and there are many well-oriented molecular chains, which look like "fibrillar clusters" on each layer and they are perpendicular to the impact direction. Finally, the expanding lay-


Figure 4   Oriented fibrillar clusters are perpendicular to the impact direction on the fracture surface of plasticized supertough nylon 11.

ers are torn, and the edge of the torn layers becomes corrugated and coiled (see Figs. 3–5). This phenomenon cannot be explained either by the multiple-crazing mechanism or by the shear-yielding mechanism.
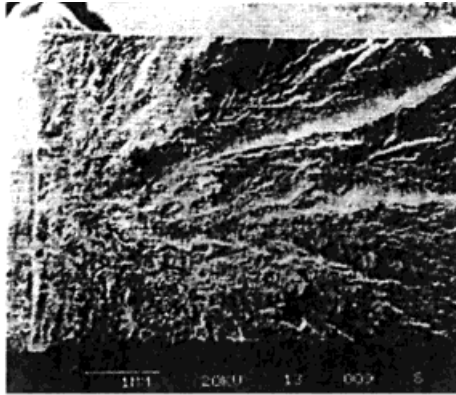
From the above facts, this fracture morphology is not similar to that of the usual crazing with the shear-yielding mechanism. A similar morphology can be observed in supertough nylon 6 blends (see Figs. 6–10). It can be concluded that a similar fracture behavior and mechanism observed in this study commonly exists in supertoughed nylons.
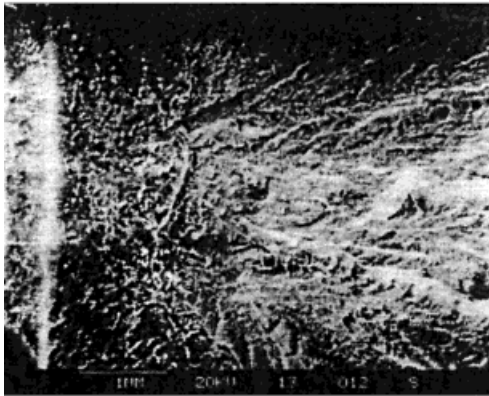
Mechanism of Multilayer Crack Extension

The so-called multilayer crack extension mechanism was put forward on the basis of the above experimental results:

Figure 3   Fracture morphology of plasticized supertough nylon 11.
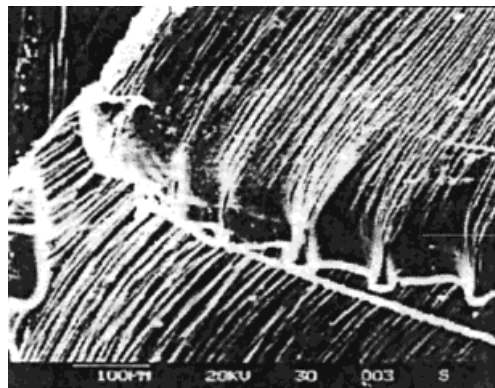
Figure 5   Corrugated and coiled fracture surface of plasticized supertough nylon 11.
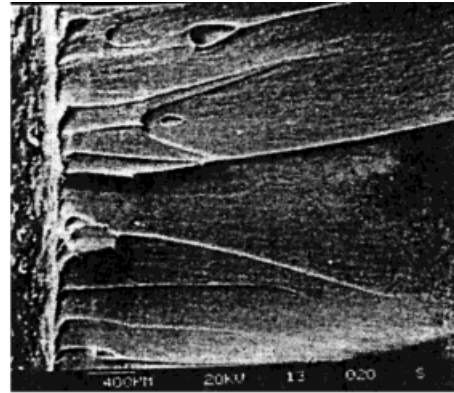
(a) One Side of fracture surface
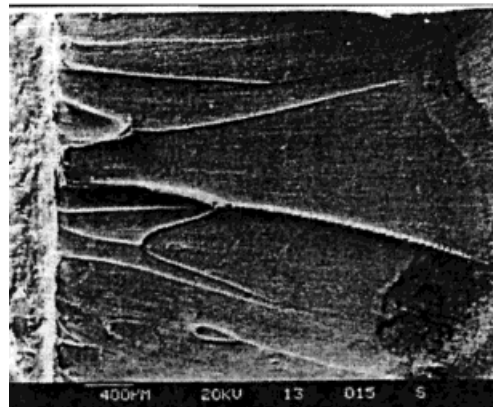

(b) The other Side of facture surface

Figure 6 Morphology of brittle fracture of nylon 6 blends, where nylon 6/MBS = 80/20.

1. Plasticized nylon 11 specimens will not break even if a great impact energy is absorbed; they show a supertough behavior.
2. From the SEM micrograph, it can be seen that the ductile fracture presents interlaced distorted laminae (Figs. 3, 5, 7, and 8). The fracture layers are corrugated, and the distorted laminae are arrayed like canine teeth.
3. On the laminae, there are many oriented "fibrillar clusters," which are perpendicular to the impact direction (Figs. 4 and 9). In the deepened layer, however, no oriented "fibrillar clusters" or only very weakly oriented fibrillar clusters are observed.

Certain microcrystal particulates and failure points exist in the plasticized nylon 11. As stress-concentration points, these points induce a multilayer microcrack like a "cavity area." When the microcracks develop further, a large crack will be generated; they will result in brittle fracture, but in this blend system, this kind of phenomenon do not appear. The edge of the upper layers in the cavity area connect with that of the down layer
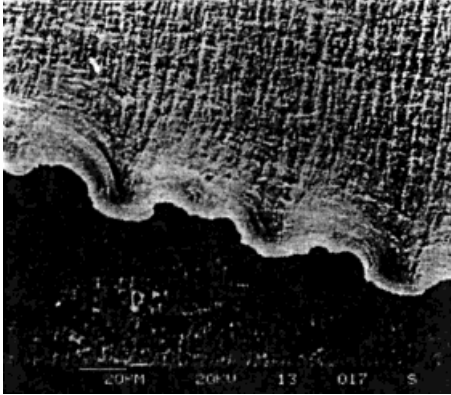

(a) One Side of fracture surface

(b) The other Side of fracture surface

Figure 7 Morphology of supertough nylon 6 blends, where nylon 6/MBS/epoxy = 80/20/5.

Figure 8 Corrugated and coiled edge of the torn layer in supertough nylon 6 blends.

"face to face," which prevents the failure of the cavity area. When the specimens are strongly impacted, the upper layers in the cavity area are pulled up. As the free volume of plasticized nylon 11 increases, the glass transition temperature of nylon 11 decreases; conversely, the flexibility of the molecular chains increases. With the layers in the microcavity area being pulled and extended, the molecular chains in the center of the layers are extended completely under the tensile stress, and the flexible molecular chains are well-oriented along the direction of the strain.

Tension causes the layers in the "cavity area" to be developed into a parabolalike side. This parabola side is opposite to the other side in the cavity area; it looks like a "cavity ellipse." When the impact energy is higher than is the surface energy of full extension and the energy of the molecular orientation, the layers in the cavity area are torn apart at the edge.

From the above-mentioned results, the "multi-layer crack extension" mechanism including the following stages is put forward:

1. The initiation of a multiple microcrack and the formation of a cavity area.
2. The formation of "connected layers" in the cavity area under the stress.
3. The extension of a connected layer in the cavity area.
4. The orientation of the molecular chains in the connected layer.
5. The split of the connected layer.

Each of the stages above dissipates much of the impact energy. In the third and fourth stages, large amounts of the impact energy are turned into "surface extension energy" and "molecular orientation energy." As the molecular clusters are oriented, the extension of the layers absorbed much energy. The development of a large crack is greatly hindered, and the impact strength is improved greatly. It results in supertoughness.

Only when a very high crack propagation energy is overcome can the material be destroyed. The extension degree of the "connected layers" and the orientation degree of the molecular chains determine the impact property of the materials. When the extension degree of the "connected layers" and the orientation degree of the molecular chains increase, the impact strength is improved. On the other hand, a fin-type brittle fracture will occur if the connected layers of the cavity area cannot extend. The extension of the connected layers and the orientation of the molecular chains depend on the plasticizing efficiency. So, the higher the plasticized efficiency is, the higher the impact strength is.

The fracture mechanism of supertough nylon 6 blends is similar to that of the plasticized nylon 11, but the cavity area generated in the first stage results from craze propagation. The developing process of the multilayer crack extension mechanism is shown in Figure 10.

CONCLUSIONS

The impact strength of nylon 11 is improved dramatically with the addition of the P1 and P2 plasticizers. Small amounts of the plasticizers can effectively increase the impact strength of nylon 11, and the contents of the plasticizers, which
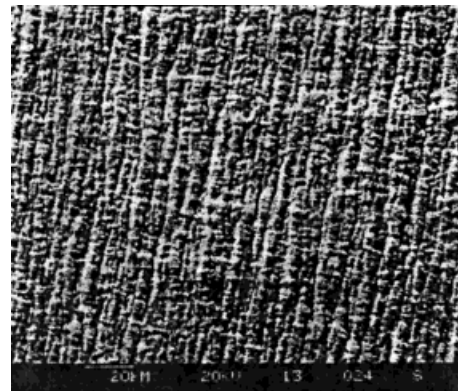
Figure 9 Morphology of the oriented fibrillar clusters, which are perpendicular to the impact direction, on fracture of supertough nylon 6 blends.
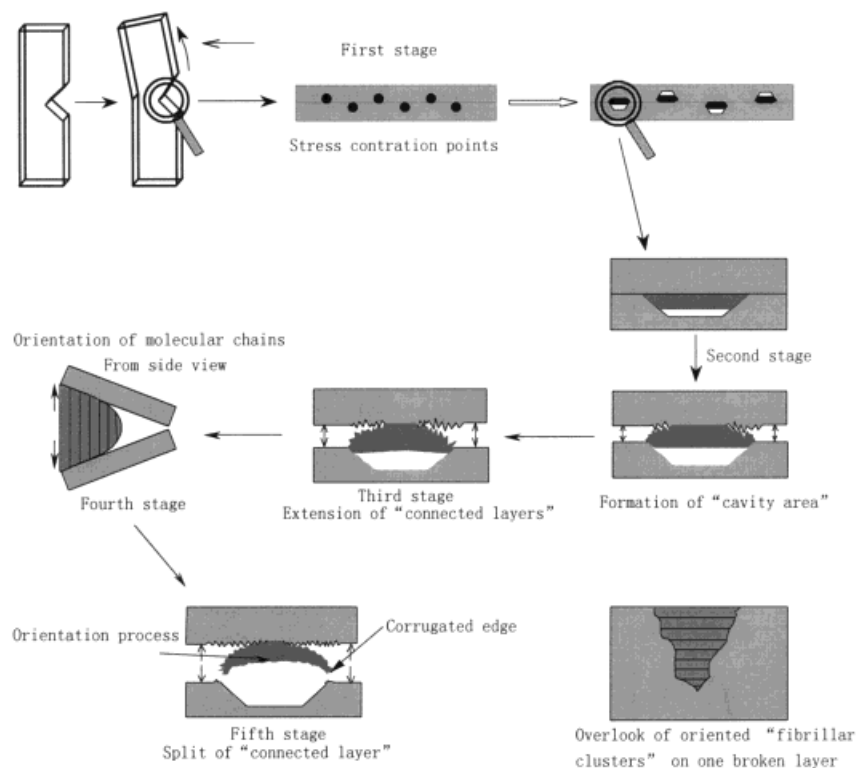
Figure 10 Illustrion of multi-layer crack extension mechanism.

result in a ductile–brittle transition phenomenon, vary with different kinds of plasticizers. The ductile–brittle transition occurs within the range of 4–6% P1 plasticizer, while the ductile–brittle transition of the nylon 11/P2 blend is generated in the vicinity of 15% P2 content. The tensile strength and tensile modulus are not sharply decreased with the addition of the plasticizers.

Based on the experimental results, the multilayer crack extension mechanism is put forward. There is the existence of certain microcrystal particulates and failure points in the plasticized nylon 11. As stress-concentration points, these points induce multilayer microcracks and quickly develop into a microcrack cavity area, each layer interlaced; the edge of the layers in the cavity area connect with each other "face to face," which results in the formation of connected layers which prevent further development of the cavity area. Under the extension strain, the interconnected layer is pulled up and extended completely, whereas the molecular chains in the connected layers are well-oriented along the direction of the strain. When the impact energy is higher than is the surface energy of the full extended layer and the orientation energy of the molecular chains,

the connected layer is torn apart. It is different from the commonly observed craze-shearing band mechanism. The impact property of plasticized nylon 11 depends on energy consumption of the extended connected layers, the orientation of the molecular chains, and the segment in the connected layers.

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