Properties of a Mechanically Processed Polymeric Material

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SYNOPSIS

A *semi*crystalline polymer, polyamide, was processed using a new technique. The technique is that of mechanically grinding the material using large inputs of energy at temperatures below the glass-transition temperature and then later reconstituting the material by applying pressure and holding at a temperature below its melting point for a period of time. This technique is normally known as mechanical alloying and only very recently has been applied to polymeric materials. The mechanical properties of strength, ductility, toughness, and hardness of polyamide material processed by this technique are investigated and compared with those of polyamide material processed by other techniques. The results indicate that altered mechanical properties occur with specific enhancements. This means that useful structural components can be made from polymers using this processing technique. The analysis of x-ray diffraction, nuclear magnetic resonance, scanning electron and optical microscopy suggests that this process has resulted in considerable alteration of both crystal structure and microstructure of this polymeric material. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polymers are widely used today because of their low density, relatively low cost, and the ability to be modified to meet a variety of preferential characteristics. The conventional techniques used to process polymeric materials all rely on heating the polymer to a point where it will flow at a reasonable rate under an applied stress such as extrusion, injection molding, or reactive injection molding (RIM) processes. However serious limitations are found in these processing techniques. High temperature polymers, such as polyimides and aromatic polyesters, etc., retain their solid nature up to the point of degradation.[1] Ultra high molecular weight polyethylene is intractable by conventional processing techniques because of its extremely high molecular weight and high melt viscosity. Also new polymeric alloys that are actively studied at present cannot be made using conventional melting techniques because of the phenomenon of phase separation that is a result of thermal incompatibility between different polymers.[2] To date, a number of techniques have been developed to process polymeric materials and polymeric alloys. Among them, mechanical alloying is one of the newest techniques currently under development by the authors.

The term mechanical alloying describes a unique type of material where its properties are obtained from specialized mechanical processing. Materials that are made by mechanical alloying are first introduced into a high energy shaker ball mill and are ground over a long period of time to produce an extremely fine powder. The powder results from a mechanism of repeated fracturing and cold welding.[3] The powder is then consolidated below the melting point temperature of the material by using pressure, time, and temperature combinations. This technique was developed in 1968 at INCO's Paul D. Mericaa Research Laboratory[4] as part of a program to produce an alloy combining oxide dispersion strengthening with gamma prime precipitation hardening in a nickel-based superalloy intended for gas turbine applications. Since then it has been successfully applied to produce many kinds of metallic alloys with resulting special properties.

Considerable effort has been made recently to apply this technique to polymeric materials. Preliminary studies[5-7] have shown that several kinds of thermoplastic polymers, including polyamide, polyethylene, polypropylene, and acrylonitrile-bu-

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tadiene-styrene (ABS plastic) can be ground into extremely fine powders using a specially designed high energy shaker ball mill. These polymeric powders can be consolidated well below their melting temperatures. Alloys of polyamide/polyethylene, polyamide/ABS with special structure and properties have been successfully produced using this technique.

The main objective of this work is to study the characteristics such as powder morphology, crystal structure and microstructure, and to evaluate the mechanical properties of polyamide material processed by the mechanical alloying technique. The comparisons of material properties with those of polyamide processed by other processing methods are given. Also the strengthening mechanism is explained by analysis using infrared spectroscopy and formic acid dissolution testing. Because only one polymer instead of two or more polymers was used in this study, polyamide material processed by this technique is defined as mechanically processed polyamide and this technique is defined as the mechanical processing technique.

EXPERIMENTAL

Material

The material used in this study is a type of semicrystalline polymer, polyamide (nylon 6,6) donated by Du Pont Inc. A batch of mechanically cut polyamide powders with an average particle size of 200 microns was also provided from Du Pont Inc. and were used for a parallel comparative study.

Mechanical Milling

Reactor grade polyamide pellets were processed in a specially designed shaker ball mill (see Fig. 1). The ball mill has an overall acceleration of 12.3 g while operating at a frequency of 29 Hz. The atmosphere inside the processing chamber was not controlled at this time but rather consisted of an air environment. The ball mill chamber was cooled using liquid nitrogen to a temperature below −150°C which is about 100°C lower than the material's glass-transition temperature. Polyamide pellets were processed for 24 h at the end of which time the powder was removed for consolidation.

Consolidation

The polyamide powder was then transferred to a consolidation press where it was heated to 80°C under vacuum condition for 20 h to degas the material. Following this the temperature was raised to 233°C and a pressure of 68.95 MPa was applied for a period of 48 h. At the end of this time a solid billet had formed and was removed from the consolidation press.

A series of consolidating experiments were carried out for mechanically processed polyamide powders. The lowest consolidation temperature for this material was found to be 100°C which is 160°C lower than its melting temperature of 260°C. However, the lowest consolidation temperature for mechanically cut polyamide powders and thermal melt polyamide pellets under the same consolidating conditions were 233 and 285°C, respectively. The degree of low temperature consolidation of mechanically processed polyamide is an unexpected phenomenon. This means that polymeric materials can be mechanically alloyed and consolidated without losing their special properties. In addition polymeric materials can be produced in a manner that can reduce the heat degradation and improve the potential for scrap recovery. Additionally, it can make the processing of materials easier. Likely new uses will evolve as the process becomes better known.

Polishing and Etching

Solid billets of polyamide were cut and mounted in thermoset plastic with the longitudinal and trans-

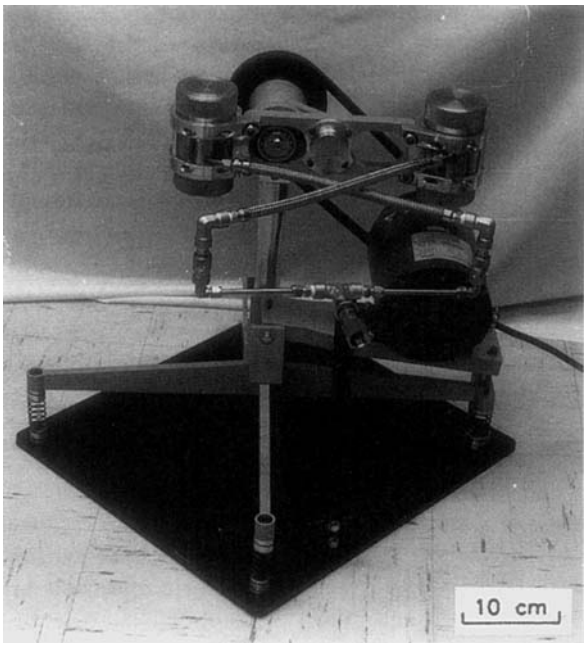

Figure 1 Shaker ball mill with insulation removed.

verse surface exposed. The exposed surfaces were ground and polished mechanically with a Buehler Ecomet 3 grinder-polisher using the following sequence: 400 grit, 600 grit, 6 μm, 1 μm, and finally 0.05 μm.

A number of etching techniques were developed and evaluated in order to provide good identification of the microstructure. It was found that the best etchant for polyamide material is concentrated xylene regent and the etching condition is 4 min at 75°C.

TESTING METHODS

The morphology of mechanically processed polyamide powder was examined with a Cambridge Scanning Electron Microscope (SEM), S100 after sputter coating powders with gold. The formic acid dissolution testing was conducted by machining specimens of polyamide materials processed by different techniques with the size of 3.5 × 3.5 × 15 mm and weight of 0.4 g. Specimens were then put in several beakers each containing 100 mL of formic acid solution, and time was recorded to the point where the specimens were totally dissolved.

A compressive stress–strain testing was performed using an MTS system Model 810 to evaluate the strength and ductility of materials. Cylinder-shaped specimens 7.0 mm in diameter and 20 mm in length were used for the test. Charpy impact testing was conducted based on ASTM standard E23. Standard size notched specimens of 10 × 10 × 55 mm were machined for testing. The impact energies obtained from the impact tester were normalized for the exact specimens thickness and reported as relative impact energy (J/m). Five specimens of each sample were used for the compressive stress–strain and impact testing and average values of ultimate strength, elongation at breakage, and impact energy were obtained. All tests were conducted at room temperature.

Hardness measurements were performed using a 100-kg load according to ASTM standard 785 (D scale) on a Service Diamond Hardness Tester, Model 8SSA. The specimens were first polished roughly to a smooth surface. At least five different points were measured and the average values of tests are reported.

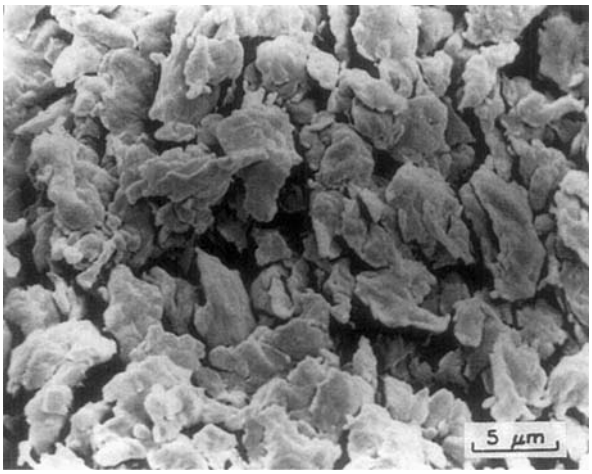

Figure 2 Powder morphology of mechanically processed polyamide material after 24 h of processing.

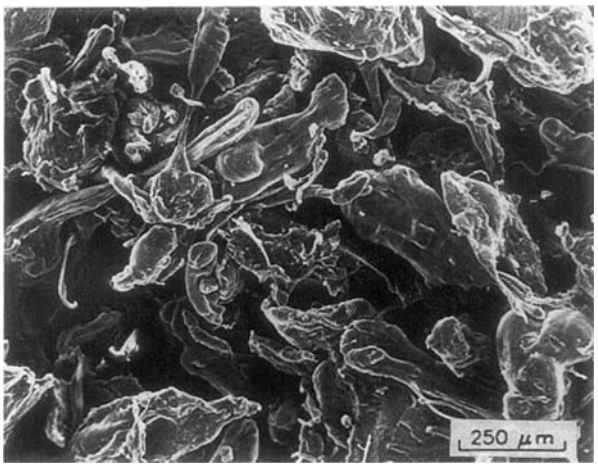

Figure 3 Powder morphology of mechanically cut polyamide.

RESULTS AND DISCUSSION

Powder Characteristics

Typical powder morphologies of mechanically processed polyamide and mechanically cut polyamide powders are shown in Figures 2 and 3. It was found that mechanically processed polyamide powder is comprised of a conglomeration of larger particles being made up of many fine, small-sized particles. Thus the overall average individual particle size is 3 microns. The powder characteristics of mechanically cut polyamide powder are quite different (see Fig. 3). The particle size is quite large (around 200 microns) and clear boundaries of the particles are apparent. Therefore, it appears that the mechanism of repeated fracturing and cold welding has resulted in the process of mechanical alloying because of the conglomeration of particles and a very coarse par-

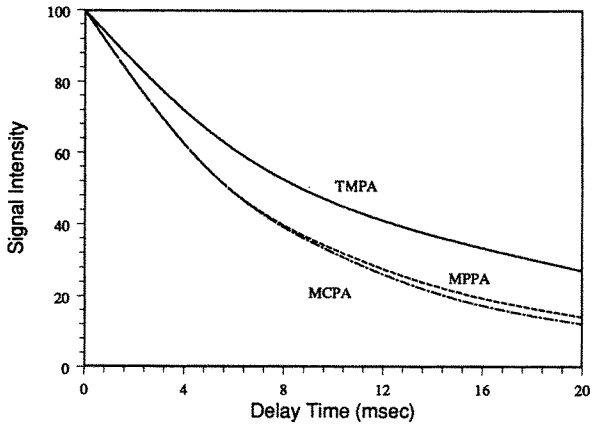

Figure 4 The analysis of ^{13}C solid state NMR of polyamide materials.

ticle shape instead of a sharply defined shape produced by other processing methods such as mechanical cutting, filing, etc. Special reactions between the molecules of mechanically processed polyamide are expected based on powder characterization.

X-Ray Diffraction Behaviour and The Measurement of ^{13}C NMR

X-ray diffraction is a powerful analytical tool that is used to determine the crystal structure and relative crystallinity of polymers. The other method to measure the relative crystallinity of polymers is the carbon-13 solid state Nuclear Magnetic Resonance (NMR) technique that has been developed recently. In order to study the crystal structure and relative crystallinity of polyamide material processed by different processing methods, both techniques were used in this investigation. The results of ^{13}C solid state NMR measurement of mechanically processed polyamide (MPPA) material consolidated at 233°C, mechanically cut polyamide (MCPA) material consolidated at 233°C, and regular thermal melt polyamide material (TMPA) consolidated at 285°C are shown in the Figure 4. The technique of ^{13}C solid state NMR works by means of inserting a delay signal time after proton–carbon cross polarization to measure the relative crystallinity of polymers. Signals from amorphous materials delay more than those from crystalline materials. Thus larger remaining signals imply higher crystallinity. From Figure 4 it is clear that TMPA material has much higher crystallinity than that of MPPA or MCPA materials. The crystallinity of MPPA and MCPA materials are almost the same which is not surprising because their consolidating conditions are the same and hence each experiences the same thermal processing conditions.

Similar results were obtained from the analysis of x-ray diffraction of the materials (see Table I). The peak intensities of TMPA material that reflect the relative crystallinity of the polymer are much higher than those of MPPA and MCPA materials. The peak intensities of MPPA and MCPA materials are almost the same. Table I also indicates other characteristics, one peak is missing, the other peak is shifted and broadened for the MPPA material compared to both TMPA and MCPA materials. This means that the mechanical processing technique has resulted in a large alteration of the crystal structure due to special reactions between molecules. For MCPA material, even though the peak position ($2T$ Angle) and space are the same as TMPA, the sequence of the high absorbed peak is changed. Therefore, it can be concluded that the different processing methods result in different crystal structure of this polymer.

Density

The results of density measurement for polyamide materials produced by different techniques are shown in Table II. It seems that TMPA material has the highest density and MCPA material has the lowest density among three types of polyamide materials but the difference in density is not very great. TMPA material has the highest density and was

Table I X-Ray Diffraction Behaviour of Polyamide Materials

Material	$2T$ Angle	Space (D)	Intensity
Mechanically processed polyamide (233°C)	27.192	3.8050	1780
Mechanically cut polyamide (233°C)	27.523	3.7602	1720
	23.731	4.3500	996
Regular thermal melt polyamide (285°C)	27.710	3.7353	1450
	23.569	4.3796	2110

Table II Density Measurement of Polyamide Materials Processed by Different Techniques

Materials	Consolidation Temperature (°C)	Density (g/cm^3)	Difference in Density Based on MCPA Material (%)
Regular thermal melt polyamide (TMPA)	285	0.967 ± 0.001	3.9
Mechanically processed polyamide (MPPA)	233	0.946 ± 0.001	1.7
Mechanically cut polyamide (MCPA)	233	0.930 ± 0.001	—

consolidated at a temperature much higher than that for MPPA and MCPA materials. Because polymers have long chain structure, the activation energy for diffusion of polymers is much higher than that of small molecule materials like metals and ceramics. Thus the molecular diffusion movement in polymeric materials strongly depends on temperature. With higher consolidation temperature, the higher mobility of molecular segments and chains will result in material with higher density. However, the densities for MPPA and MCPA materials should be the same because they are consolidated under the same conditions. MPPA material having a higher density indicates that the mechanical processing technique has resulted in special reaction and higher surface tension on polyamide particles; therefore a material with higher density is produced.

Microstructure

Figure 5 is an optical micrograph of TMPA material. It is in general agreement with the features of similar material published by others.[8] It shows grain size of approximately 50 microns. The microstructure of MCPA is shown in Figure 6. It is found that the grain distribution is not even and the average grain size is around 200 microns, which is close to its powder particle size. However, the microstructure of MPPA material is completely different (see Fig. 7). For MPPA material, the grain boundary is not clearly defined and the domain size is very small (around several microns) especially when compared to TMPA and MCPA materials. The etchant attack is not uniform but is local to specific regions. The reason why MPPA material has this kind of microstructure is not clear at this time but is likely due to the special reactions between polyamide molecules resulting from the mechanical processing.

Mechanical Property Evaluation

Hardness

Table III shows the results of hardness measurements. It is surprising that the hardness of MPPA and MCPA materials are much higher than that of TMPA material because the latter has the highest degree of crystallinity.

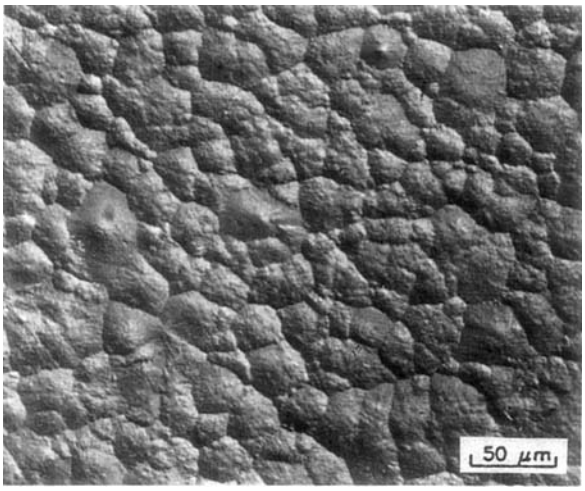

Figure 5 Optical micrograph of regular thermal melt polyamide.

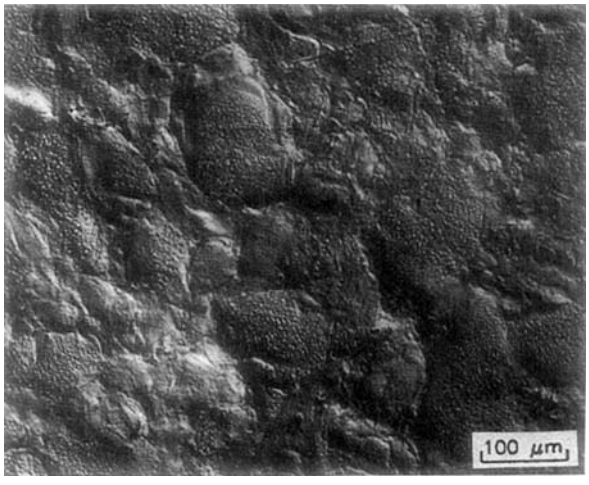

Figure 6 Optical micrograph of mechanically cut polyamide.

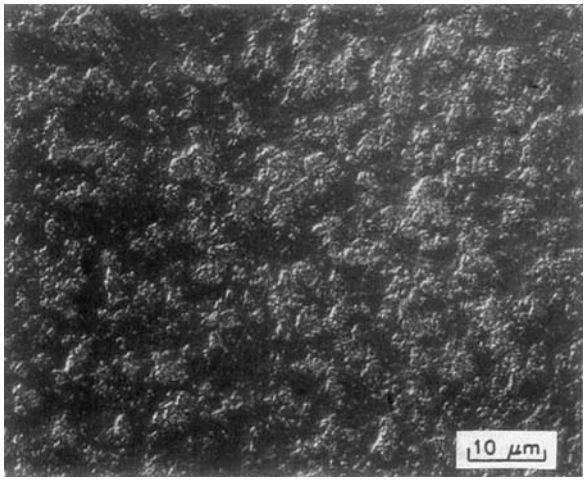

Figure 7 Optical micrograph of mechanically processed polyamide.

Among the three kinds of polyamide materials, MPPA material has the highest hardness. As MPPA and MCPA materials were consolidated at the same condition and have almost the same crystallinity, this suggests that the mechanical processing technique can produce a much stronger material.

Strength, Ductility, and Impact Energy

The results of compressive stress–strain tests are shown in Table IV. It was found that the ultimate strength of MPPA material has an increase of 20% compared to TMPA material and 40% compared to MCPA material. MPPA materials with even higher strengths can be obtained when consolidated at higher temperatures but still lower than its melting point temperature.[6] In the comparative study conducted here, the ductility of MPPA material is 30% lower in comparison to TMPA material. When compared to MCPA material, an increase of 43% in ductility is observed. Figure 8 shows that the impact strength of both MPPA and TMPA materials based on ASTM standard E23. It is found that the toughness of MPPA material has an increase of 40% compared to that of TMPA material even though its ductility is lower than TMPA material. This is really an unexpected result although the reason is not clear at this stage. However, the end result is very encouraging. Thus it can be concluded that the mechanical processing technique can strengthen and toughen polymeric materials and still retain a fair degree of ductility. This means that useful structural components can be made using this technique, and that the potential for obtaining even better properties exists once this process has been more thoroughly explored.

Strengthening Mechanism

The poor properties of the MCPA material is thought to occur due to the degradation of molecular chains during the processing. However, the reason why the mechanical processing technique acts to strengthen the material is not clear. To understand this, it is necessary to study the processing details of this technique. In the procedure of mechanical processing, polymers are put into a high energy ball mill to produce extremely fine powders under the mechanism of repeated fracturing, cold welding, and refracturing as a result of constant collision of steel balls. After a long processing time, the rates of cold welding and fracturing are in balance and extremely complicated interactions between the molecules of the polymers are expected to occur.

These interactions can be divided into two types. One is a chemical reaction, the polyamide molecule may react with oxygen in the air environment or some graft copolymerization reaction between polyamide molecules could happen under the condition of high energy compaction and a cross-linked network structure could result. This high energy compaction could result in the local instantaneous temperature reaching several hundred degrees Celsius at some specific points in the particles.[9] This kind of reaction can be detected by infrared spectroscopy. The other type of interaction is physical interpenetrations at the molecular level between random amorphous areas and lamellar crystal areas (see Fig. 9). This can be proved by formic acid dissolution testing. If polyamide materials can be dissolved in formic acid solution, this means no chemical reac-

Table III Hardness Measurements (ASTM D785)

Materials	Consolidating Temperature (°C)	Hardness
Mechanically processed polyamide	233	89 ± 1
Mechanically cut polyamide	233	82 ± 1
Regular thermal melt polyamide	285	79 ± 1

Table IV Mechanical Properties of Compressive Stress–Strain Tests

Material	Ultimate Strength (MPa)	Elongation (%)
Mechanically processed polyamide	146.38 ± 0.50	24.9 ± 0.3
Mechanically cut polyamide	104.50 ± 3.17	14.3 ± 0.5
Regular thermal melt polyamide	125.35 ± 2.60	34.3 ± 3.0

tion exists between molecular long chains. The difference in dissolution time only indicates that the degree of physical interaction between polymeric molecules are different. Whereas, if formic acid is found not to be a solvent of polyamide material, it shows chemical reactions, probably graft copolymerization or chemical network structure, as a result.

The analyses of infrared spectroscopy have been carried out on MPPA powders produced in air and argon gas environments and on TMPA material. No differences were observed from these three spectroscopies.[6] However the results from formic acid dissolution tests (see Table V) does indicate that the mechanical processing technique results in the strongest physical interactions between polymer molecules among three kinds of processing methods because longer time is needed to dissolve this material. It is also found from Table IV that the increasing percentage of specimen dissolved time for MPPA material is also reflected by the interaction strength between molecules as seen by the response of the increased percentage of strength and toughness of this material. This strongly suggests that the physical interpenetration mechanism plays an important role in strengthening and toughening MPPA material. This suggestion can be further supported by the evidence of alterations of crystal structure and microstructure of MPPA material compared to the other two types of polyamide materials. The interpenetration of polymer molecular long chains in amorphous and crystalline areas results in changes as measured by the x-ray diffraction study. The processing changes the crystal structure of the polymer that results in only one broad peak as well as a slight shifting of this peak on x-ray diffraction recordings for the MPPA material. Two main peaks occur for TMPA and MPPA materials. Because of the existence of the interpenetration in this semicrystalline polymer, the crystal area may act as a "cross-linking point." This in turn will restrain the movement of molecular segments and a stronger but relatively more brittle material will result. The microstructural characterization showing no clear grain boundary for MPPA material is thought to be a result of the physical interpenetration phenomenon.

CONCLUSIONS

This study shows that polyamide material can be ground into extremely fine powders (3 microns) us-

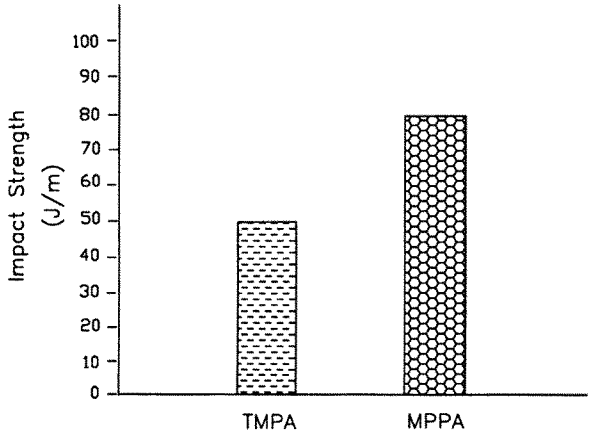

Figure 8 Comparison of the impact strength of regular thermal melt polyamide (TMPA) and mechanically processed polyamide (MPPA).

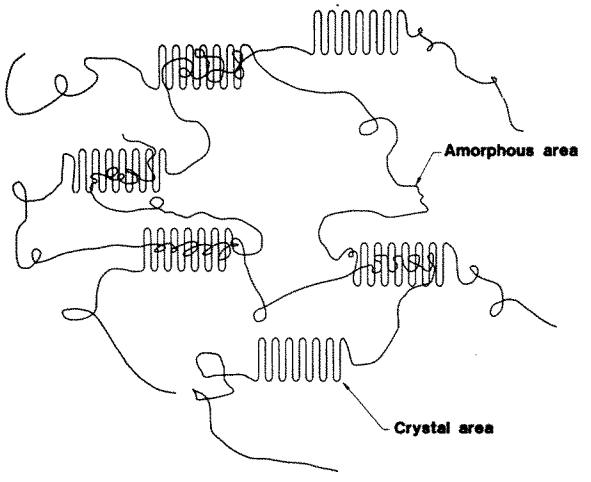

Figure 9 Interpenetration of molecular chains in the amorphous and crystal areas.

Table V Results of Formic Acid Dissolved Test

Materials	Specimen Weight (g)	Solution Time (min)	Increasing Dissolved Time Based on TMPA Material (%)
MPPA	0.4	36	44
MCPA	0.4	30	20
TMPA	0.4	25	—

ing the mechanical alloying technique. The process is based upon the mechanism of repeated fracturing, cold welding, and refracturing. This is achieved using a specially designed high energy shaker ball mill. Mechanically processed powders can be consolidated well below the material's melting temperature using a combination of time, temperature, and pressure. The lowest consolidation temperature for mechanically processed polyamide material is found to occur at 100 instead of 233°C for mechanically cut polyamide and 285°C for regular thermal melt polyamide. This low temperature consolidation is a new unexpected phenomenon for polymers. The improvement of strength and toughness of mechanically processed polyamide material is probably due to the higher degree of physical interpenetration on the molecular level of polymers between amorphous and crystalline areas when compared to other processing techniques. However, the ductility of mechanically processed polyamide has been reduced compared to regular thermal melt polyamide. The study of optical microscopy and x-ray diffraction indicate that the mechanical processing technique results in definite alterations of the microstructure and crystal structure. This alteration is different from the regular thermal melt processing technique and mechanically cut technique.

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