

Effects of Processing Parameters on Material Properties of Mechanically Processed Polyamide

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SYNOPSIS

A semicrystalline polyamide polymer was processed using a new technique known as mechanical alloying. The material processed by this technique was first introduced into a high-energy ball mill and ground over long periods of time, resulting in the production of extremely fine powders. These powders were subsequently consolidated well below the materials' melting-point temperature. The effect of processing parameters including mechanical milling time, consolidation temperature, and the length of consolidation time were studied fairly extensively. The investigation shows that polyamide powders are continually refined with increasing mechanical milling time and the resulting materials have improved mechanical properties. The influence of both consolidation temperature and the length of consolidation time on material properties indicate that materials with higher density, crystallinity, hardness, strength, and ductility are produced when consolidated using higher temperatures and longer times. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Today, the most popular techniques used to process polymeric materials are extrusion, injection molding, reactive injection molding, blow molding, and casting. The commonality of these processing techniques all rely on heating the polymers to a point where they can flow at a reasonable rate under an applied stress. However, serious limitations are found in these techniques when processing high-temperature polymers and polymers with extremely high molecular weight.¹ Also, new polymeric alloys which have more attractive properties as compared to single-component polymers cannot always be produced by using a conventional melt-blending technique. This is because most polymer pairs are immiscible at the molecular level due to the very low entropy and enthalpy of mixing of macromolecules. A common method to solve this problem is to introduce a chemical reagent, known as a compatibilizer, to provide a bridge between the immiscible polymer blends. Even though this type of chemical method can be used to produce a polymeric alloy, sometimes it is

difficult to find a suitable compatibilizer for specific polymer pairs.

Previous investigations have been carried out to process polymers by a technique similar to that used in the powder metallurgy industry.²⁻⁷ Products are made by cold molding at very high pressures followed by a sintering cycle. The sintering temperature is generally set near the materials' melting point. The advantage of this processing method is that a "clean" polymer part can be produced since this technique does not require the polymer to flow on a macroscopic scale. This reduces or eliminates the need for thermal stabilizers, lubricating agents, and other processing aids. Improved mechanical properties were claimed in some of these investigations. Studies from Stott^{2,3} indicated that polyamide material can be processed using this technique and superior physical properties could be obtained as compared to materials molded using traditional processes involving mixing with a high volume fraction of fillers. However, it was pointed out that only polyamide powders prepared by chemical precipitation can be used with this method. Satisfactory results were not obtainable for polyamide powders made by mechanical grinding molding pellets and it was

not felt that materials produced in this manner would work.

Recently, a new kind of processing technique used to produce both polymers and polymeric alloys without the addition of any chemical reagents was conceived by Shaw in 1988⁸ and later was initially developed by the authors. This technique is known as mechanical processing and mechanical alloying of polymers.

The mechanical alloying technique was developed in the late 1960s at INCO's Paul D. Merica Research Laboratory⁹ during a program to produce an alloy-combining oxide dispersion strengthening with gamma prime precipitation hardening in a nickel-based superalloy intended for gas turbine application. Materials that are made by this technique are first introduced into a high-energy ball mill and are ground over a long period of time to produce an extremely fine, evenly distributed powder. The powder forms as a result of a mechanism of repeated fracturing and cold welding.¹⁰ The powder is then consolidated below the melting-point temperature of the material by using pressure, time, and temperature combinations. Today, the mechanical alloying process is not restricted to producing complex oxide dispersion-strengthened (ODS) alloys. It has become a means for producing composite metal powders with controlled, extremely fine microstructures. Consequently, it can be used to produce alloys that are difficult or impossible to produce by conventional techniques.

The idea of being able to create mechanical alloyed polymers stems from the good success achieved using metals and a number of basic behavior characteristics associated with polymers that have similarities with metals. Preliminary studies have shown several thermoplastic polymers, such as polyamide (PA), polyethylene (PE), polypropylene (PP), polystyrene (PS), and acrylonitrile-butadiene-styrene (ABS), can be processed using the mechanical alloying technique with improved mechanical properties and special structural characteristics. Alloys of PA/PE and PA/ABS have also been made successfully using this technique without introduction of any chemical reagents.^{11,12}

The powder characteristics, microstructure, and mechanical properties of PA material processed by mechanical alloying have been investigated extensively and compared with those of PA material processed by other techniques¹³ such as regular thermal melting and mechanical cutting. It was found that the mechanical alloying technique can strengthen polymeric materials. The study of optical microscopy and X-ray diffraction indicated that the mechanical

alloying technique resulted in definite alterations of the microstructure and crystal structure. This alteration was compared to the regular thermal melt-processing technique and mechanically cutting technique.¹³ A good review of the mechanically alloyed polymer work can be found in a recent publication.¹⁴

The main objective of this article was to study the influence of processing parameters including mechanical milling time, consolidation temperature, and the length of consolidation time on the fundamental characteristics of PA material. Properties such as powder morphology, macrostructure, crystal structure, density, and mechanical properties were examined. As only one polymer was used in this study instead of two or more polymers, PA material processed by this technique is described as mechanically processed polyamide and this technique is referred to as the mechanical processing technique.

EXPERIMENTAL

Mechanical Milling

The material used in this study was provided by DuPont and is a semicrystalline polymer, PA (nylon 6,6, trademark ZYTEL nylon resin). Processing of reactor-grade PA pellets was conducted in a specially designed shaker ball mill.¹³ The ball mill operates at a frequency of 29 Hz and has an acceleration of 12.3g. The atmosphere inside the processing chamber was that of an air environment. Liquid nitrogen was used to cool the ball mill chamber. A temperature of -150°C or less was maintained during processing. After specific processing times of 1, 3, 6, 12, 18, and 24 h, PA powders were removed for analysis and consolidation.

Consolidation

The method of consolidation is carried out by placing the PA powder in a cylindrical press under the application of pressure using a hydraulic ram and heating with a furnace to a specific temperature for a set period of time. Consolidation was conducted using first vacuum degassing at 80°C for a period of 24 h. Following this, the temperature was increased to various levels from 100 to 250°C . A pressure of 68.95 MPa was applied for various periods of time ranging from 8 to 48 h. At the end of the selected processing time, a solid billet had formed and was removed from the consolidation press.

Experimental Testing Methods

The microstructure of PA material was evaluated by a Zeiss optical microscope. The same polishing condition and etching techniques were used as stated in a previous publication.¹³ The powder morphology was examined using a Cambridge scanning electron microscope (SEM) S100 after sputter-coating the powders with gold-palladium. A Mettler 12E differential scanning calorimeter (DSC) was used to analyze the thermal behavior of polyamide material. The solid sample weight used was around 4 mg and the heating rate was set at 10°C/min.

An 8SSA Service diamond hardness tester was used to measure the hardness of PA materials according to ASTM standard D785 (L Scale) with a 60 kg load. The specimens were polished to a smooth surface of 600 μm . Five different measurements were then taken and both mean and standard deviation values are reported.

Cylinder-shaped specimens 7 mm in diameter and 20 mm in length were used for compressive stress-strain testing. The purpose of this testing is to evaluate the strength and ductility of the materials. This testing was conducted using an MTS system, Model 810. Five specimens for each testing condition were used and average values of ultimate strength and strain at fracture were obtained. All tests were conducted at room temperature.

RESULTS AND DISCUSSION

Effect of Milling Time on Material Characteristics

Powder Morphologies

Typical powder morphologies of mechanically processed PA after 1, 3, 6, 12, 18, and 24 h of processing were studied using the SEM and the results are shown in Figure 1(a)–(f). It is found that with increasing processing time PA powders are continually refined and particle morphology changes from large sharp shapes [Fig. 1(a)–(c)] to evenly distributed coarse-layered structures [Fig. 1(d)–(f)]. From studies of particle morphology, it appears that the mechanism of repeated fracturing and cold welding has occurred as a result of high surface reactivity and the resulting tendency of conglomeration of particles. This results in the development of small but coarse-layered particle shapes with longer processing times. After 24 h of processing, it appears that a balance between cold welding and fracturing is reached

as the powder is fairly coarse and very uniform when viewed at high magnification. Large particles are made up of many fine, small-sized particles. The average individual particle size is approximately 3 μm . Therefore, high reactivity at the interfaces between the particles of mechanically processed PA are expected based on powder characteristics.

Mechanical Properties Evaluation

PA powders processed for different lengths of time in the shaker ball mill were transferred to a consolidation press and consolidated into solid billets at 233°C under a pressure of 68.95 MPa for a period of 48 h. It should be pointed out that the melting point of this material is 265°C. A compressive stress-strain test was then conducted to evaluate the mechanical properties. The testing results (Table I) indicate that the ultimate strength and fracture strain are enhanced considerably with increasing mechanical milling time going from 1 to 12 h. The strength and ductility are found to continually increase with processing time from 12 to 24 h. However, the degree of increase is not particularly large and a plateau appears to be reached for a processing time of 24 h. The compressive stress-strain results indicate that mechanical processing time has a large influence on material properties. When mechanical processing time is short, the reactivity between particle surfaces are limited and the mechanical properties are poor. With a longer processing time, the balance between fracturing and cold welding is more closely approached. An increase in the number of interface reactions occurring from the longer processing period results in producing materials with better properties.

Solvent Dissolution Testing

A solvent dissolution test was carried out to study the change of the degree of interface reactions when increasing the mechanical milling time. The PA material was cut into a cubic shape with a size of 3 \times 3 \times 3 mm³. Three specimens of each material were then put into 100 mL of formic acid solvent and the average dissolution time was recorded.

Figure 2 shows the solvent dissolution test results of PA material processed for different lengths of time in the shaker ball mill and consolidated at 233°C for 48 h. It is found that the dissolution time of PA material increases with increasing of the mechanical milling time. This means that the degree of the interface reactions increases with longer processing

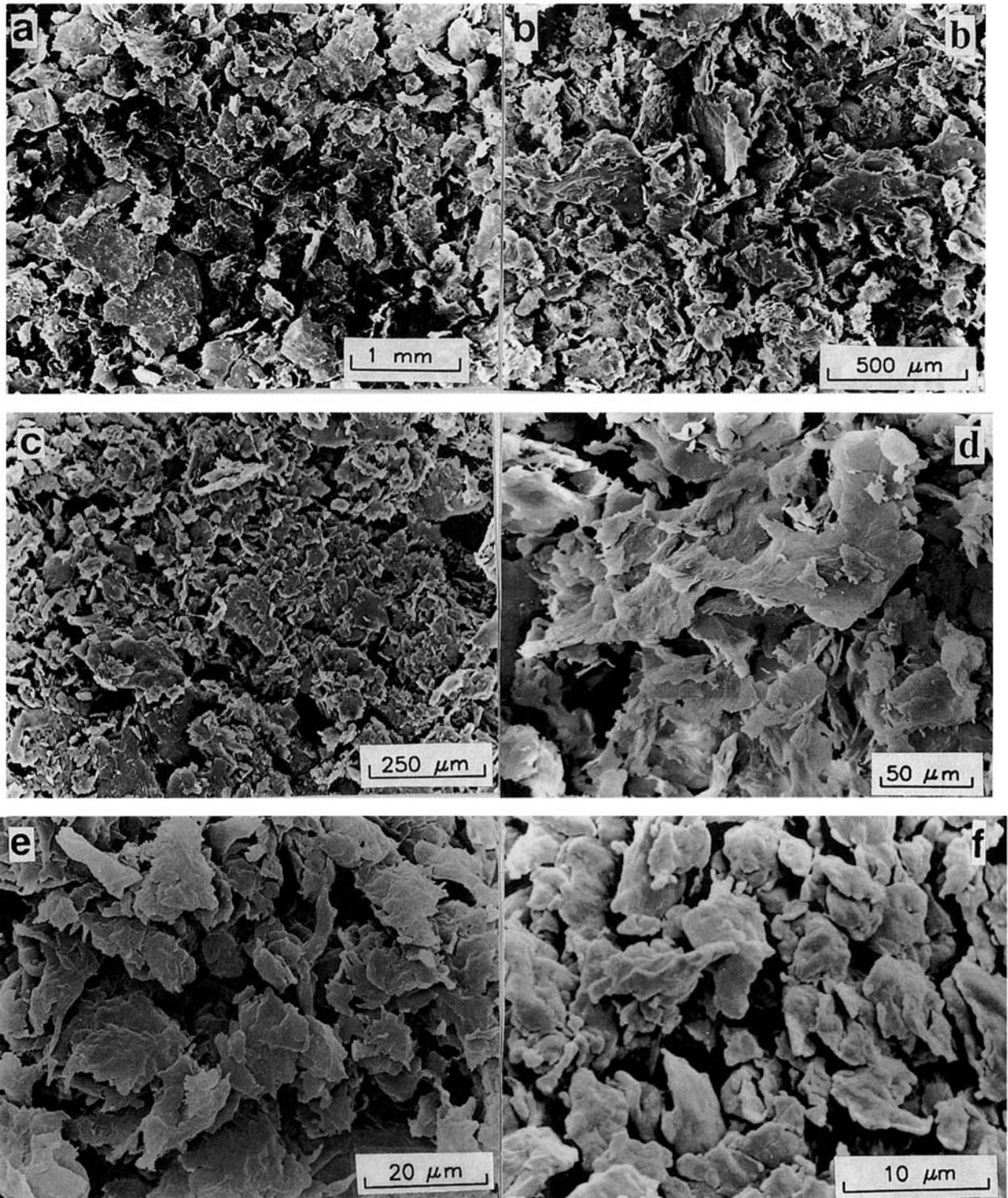


Figure 1 Particle morphology of PA powders after (a) 1 h, (b) 3 h, (c) 6 h, (d) 12 h, (e) 18 h, and (f) 24 h of processing.

Table I Effects of Mechanical Milling Time on the Compressive Stress–Strain Behavior of PA

Mechanical Milling Time (h)	Ultimate Strength (MPa)	Elongation (%)
1	101.3 ± 1.2	12.7 ± 0.9
3	119.6 ± 0.9	16.4 ± 0.8
6	133.5 ± 1.8	19.3 ± 1.1
12	141.7 ± 2.4	22.9 ± 1.9
18	145.2 ± 1.8	24.0 ± 1.0
24	146.4 ± 0.5	24.9 ± 0.3

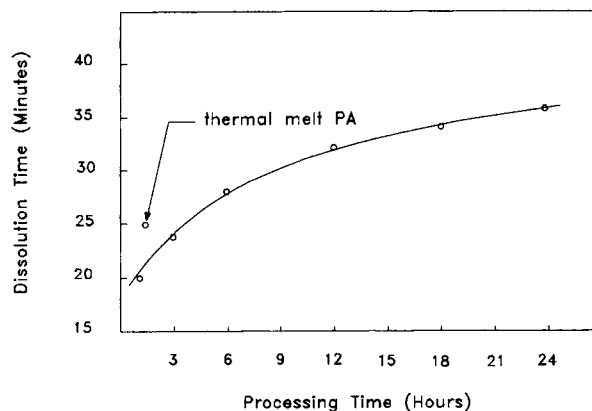
periods. Thus, materials with better properties are formed.

Effect of Consolidation Temperature on Material Characteristics

A series of consolidation experiments were carried out on mechanically processed PA powders after 24 h of attrition milling. The consolidation temperatures used were 100, 140, 185, 233, and 250°C, respectively. The low-limit consolidation temperature was 100°C, which is 165°C lower than the material melting-point temperature of 265°C. However, it was found that the lowest consolidation temperature for the reactor-grade pellets occurred at 285°C. This low-temperature consolidation of mechanically processed PA is an unexpected phenomenon. Generally, it is known that the driving force for polymeric particle bonding at temperatures below the melting point is surface tension rather than diffusion. Diffusion is the dominant mechanism in metals.¹⁵ This phenomenon shows that repeated fracturing and cold welding due to mechanical processing results in higher surface tension or highly active surfaces. This study has found that mechanically processed PA has improved in mechanical properties and developed special microstructures compared to regular thermal melt PA and, hence, it is unlikely that surface tension is the only important reaction here. Rather, the increased strength of the material must be derived from the interface reactions resulting from the repeatedly cold weld/fracturing process.

Density

The results of density measurements for mechanically processed PA consolidated at different temperatures and regular thermal melt PA consolidated

**Figure 2** The results of formic acid dissolution testing on PA consolidated at 233°C.

at 285°C are shown in Table II. It is found that the density of mechanically processed PA increases with increasing consolidation temperature. Normally, diffusion will not occur to any noticeable degree in a solid polymer; rather, the material must be melted. This means that internal energy is stored in the mechanically processed materials, which combined with some low-temperature heat energy allows diffusion or movement of the end of the chains occur. This result confirms other current work.¹⁶ The higher the consolidation temperature, the higher the mobility of molecular segments and chains. Therefore, the long-chain molecules tend to move to fill molecular voids and materials, with higher density being obtained. It should be pointed out that small voids or porosity is not apparent in these materials even when viewed at high magnifications in the SEM. Also, the high-pressure and temperature combination results in material creep, which, in turn, eliminates microscopic voids after a short period of time during consolidation. Rather, the voids or spaces are formed on a molecular level. This also means that

Table II Density of PA for Various Consolidation Temperatures

Material	Consolidation Temperature (°C)	Density (g/cm ³)
MPPA ^a	100	1.022
MPPA	140	1.070
MPPA	185	1.100
MPPA	233	1.120
MPPA	250	1.136
Thermal melt PA	285	1.167

^a Mechanically processed polyamide.

the strength-to-weight ratio of these new materials is considerably better than are the corresponding thermal melt materials.

Crystallinity

The crystal structure and the crystallinity of polymers can be determined by using X-ray diffraction and DSC testing. The analysis of X-ray diffraction information (Table III) indicates that consolidation temperature does not influence the crystal structure of PA materials. The peak positions, 2θ angle, and d space of mechanically processed PA materials consolidated at different temperatures are nearly identical. However, peak intensities which reflect the relative crystallinity of the materials are different. Increasing consolidation temperature results in materials with higher amounts of crystallinity as reflected by the intensity measurements. The crystallinity can be quantified by DSC testing. Figure 3 shows the effect of consolidation temperature on the material crystallinity. The crystallinity, X , is calculated by $X = \Delta H_f^*/\Delta H_f$ in which ΔH_f represents the heat of fusion of a perfectly crystalline polymer and the value of PA material is 196 kJ/kg.¹⁷ ΔH_f^* is the true heat of fusion of polymeric material and is measured based on the total area under the melting peak of the DSC spectrum. As shown from X-ray diffraction testing, the results from Figure 3 indicated that materials with higher crystallinity are formed when consolidated at higher temperatures.

The other information shown in Table III is the X-ray diffraction behavior of regular thermal melt PA. This material behaves quite differently compared to that of mechanically processed PA. Two absorption peaks at different d spaces are found

Table III X-ray Diffraction Analysis of PA Materials Consolidated at Different Temperatures

Material	Consolidation Temperature (°C)	2θ Angle	Space (d)	Intensity
MPPA	100	27.035	3.8267	1164
MPPA	140	27.377	3.7795	1304
MPPA	185	27.557	3.7556	1640
MPPA	233	27.192	3.8050	1780
MPPA	250	27.613	3.7481	1986
Thermal melt PA	285	27.710	3.7353	1450
		23.569	4.3796	2100

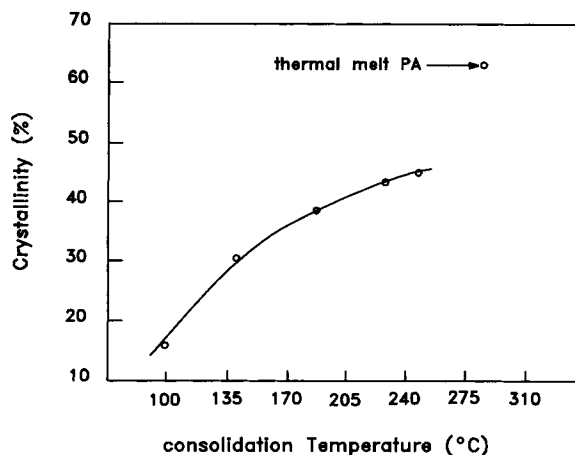


Figure 3 The effect of consolidation temperature to PA materials crystallinity for a constant time of 48 h.

rather than one peak for the mechanically processed PA. This means that the mechanical processing technique has resulted in the alteration of the crystal structure of this polymeric material.

Microstructure

An optical micrograph of regular thermal melt PA material is shown in Figure 4(a). It is typical to that found by others.¹⁸ It has the characteristic of a clearly defined spherulitic structure, with the size being on an average about 100 μm . The optical micrographs of mechanically processed PA consolidated at different temperatures are shown in Figure 4(b)–(f). A completely different microstructure is found compared to that of regular thermal melt PA. No clear grain boundary is apparent and a very small domain size is found. For mechanically processed PA consolidated at higher temperatures, it seems that a finer and more distinct microstructure has occurred.

Mechanical Properties Evaluation

Hardness. The results of hardness measurements based on ASTM Standard D785 are shown in Table IV. The hardness of mechanically processed PA increases with increasing consolidation temperature. This is reasonable as it has been shown previously that mechanically processed PA has a higher density and crystallinity when consolidated at higher temperatures. However, it is surprising that the hardness of regular thermal melt PA is the lowest compared to all the various mechanically processed PA materials even though it has the highest density and crystallinity. This indicates that stronger bonding and, hence, stronger polymeric materials can be

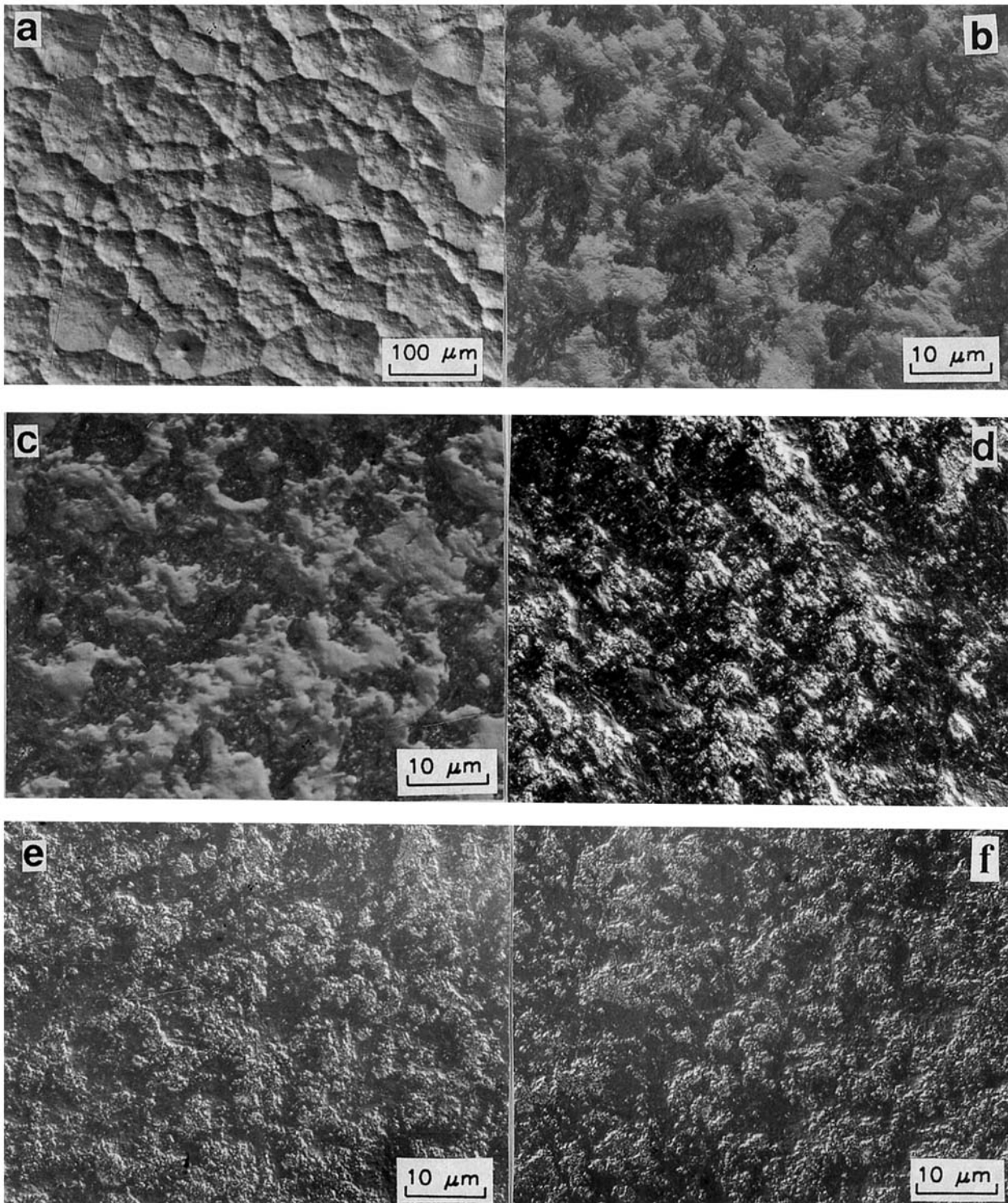


Figure 4 Optical micrographs of (a) regular melt PA and mechanically processed PA consolidated at (b) 100°C, (c) 140°C, (d) 185°C, (e) 233°C, and (f) 250°C.

produced using the mechanical processing technique. The strengthening mechanism of these materials likely results from unique interface reactions.

Strength and Ductility. Table V shows the results of compressive stress-strain tests. It is found that both ultimate strength and fracture strain of

Table IV Hardness Measurements of PA Materials Consolidated at Different Temperatures

Material	Consolidation Temperature (°C)	Hardness (ASTM 785, L Scale)
MPPA	100	86.0 ± 0.8
MPPA	140	89.5 ± 0.9
MPPA	185	92.0 ± 1.0
MPPA	233	93.0 ± 1.0
MPPA	250	95.0 ± 1.0
Thermal melt PA	285	73.5 ± 1.0

mechanically processed PA materials increase with increasing consolidation temperature. The improvement of strength is likely attributed to several factors which include higher density, higher crystallinity, and better bonding as indicated by a more distinct microstructure.

The strength of mechanically processed PA consolidated at 250°C has an increase of 30% while the ductility has been reduced by approximately 25% compared to regular thermal melt PA. Also, it is clear from Table V that most of the mechanically processed PA materials except those consolidated at temperatures lower than 140°C have higher strength compared to the thermal melt PA. This again confirms that the mechanical processing technique can produce stronger materials. Thus, this technique results in stronger bonding and acts as a method to strengthen polymeric material.

Effect of Consolidation Time on Material Properties

Density

Table VI summarizes the change in density of mechanically processed PA consolidated at 233°C for different lengths of consolidation time. Materials with higher densities are obtained when consolidated at longer times. This means that if consolidation time is not long enough, incomplete densification and bonding occurs. It was also found that when consolidation time is approximately 24 h the densities of the materials are quite close and do not improve significantly with extra consolidation time. This means that the consolidation process is for all practical purposes completed after a period of 24 h.

Table V Compressive Stress–Strain Results of PA Consolidated at Different Temperatures

Material	Consolidation Temperature (°C)	Ultimate Strength (MPa)	Elongation (%)
MPPA	100	109.3 ± 1.5	13.8 ± 1.2
MPPA	140	125.2 ± 1.3	16.7 ± 1.0
MPPA	185	144.5 ± 1.0	19.2 ± 0.8
MPPA	233	146.4 ± 0.5	24.9 ± 0.3
MPPA	250	160.4 ± 1.9	25.4 ± 1.2
Thermal melt PA	285	125.4 ± 1.0	34.3 ± 1.1

Crystallinity

The X-ray diffraction behavior of mechanically processed PA consolidated for 8, 14, 24, 36, and 48 h are shown in Table VII. No change of crystal structure was found with change in the length of the consolidation time. The peak positions or d spaces are almost identical. The intensities continually increase with longer consolidation time as the materials develop higher degrees of crystallinity. The results from DSC testing (Fig. 5) also confirm this behavior. This phenomenon is reasonable, as a polymer's long-chain structure makes it difficult to move and form crystal structures. For this mechanically processed material, when the consolidation time is longer, the molecular chain has enough time to move and higher crystallinity is expected. As a result, based upon crystallinity, materials with higher strength will form, yet the crystallinity of the mechanically processed material is considerably lower than that of the thermally melted material.

Mechanical Properties Evaluation

Hardness measurements and compressive stress–strain testing results conducted in order to evaluate the mechanical properties of PA materials consolidated at different lengths of time are shown in Table

Table VI Density of Mechanically Processed PA Consolidated for Different Times at 233°C

Material	Consolidation Time (h)	Density (g/cm ³)
MPPA	8	1.075
MPPA	14	1.102
MPPA	24	1.112
MPPA	36	1.117
MPPA	48	1.120

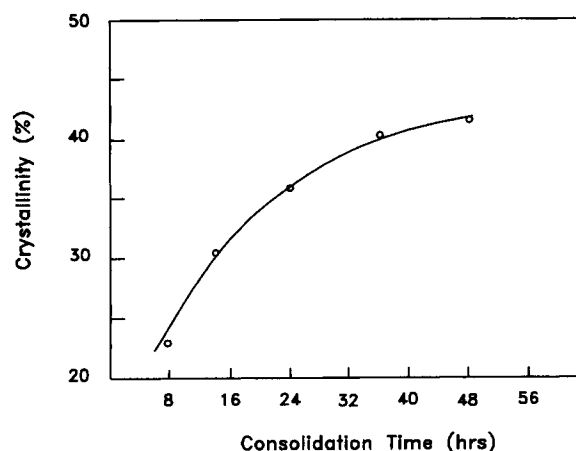
Table VII X-ray Diffraction Behavior of Mechanically Processed PA Consolidated for Different Times at 233°C

Consolidation Time (h)	2T Angle	Space (<i>d</i>)	Intensity
8	27.620	3.7472	1220
14	27.502	3.7629	1305
24	27.806	3.7226	1462
36	27.628	3.7462	1653
48	27.192	3.7050	1780

VIII. It is found that stronger and more ductile materials can be produced using longer consolidation times. The results are as would be expected since materials develop higher density and crystallinity with increasing consolidation time. Again, similar to what has been shown for density, the strength, hardness, and ductility of PA materials consolidated around 24 h tend to a limiting value. This means that consolidation is close to being finished after 24 h.

Current Understandings of Mechanisms

The effect of milling time indicates that a larger number of interfaces which form due to the cold weld/fracture process leads to stronger bonding. Thus, a higher number of reactive surfaces or peripheral areas leads to an increase in bonding strength. This is substantiated by the solvent dissolution testing results. An increase in consolidation temperature results in higher strength and density; these two behaviors are important in understanding the material interactions which are a consequence of the large increase in activity of the processed particles. Thus, the material can be looked at in terms of containing internally stored mechanical energy as a result of the processing, which combined later with elevated temperature results in an activity condition, whereby intermingling or mixing and movement of the ends of the polymer chains occurs. This means that physical interpenetrating networks are being set up due to the elevated temperature conditions and that the end of the chains are making their way through the material and tend to fill the small molecular voids. The results from X-ray diffraction and differential scanning calorimetry indicate that the *d* spacing or bonding relationship of these materials does not change with changing processing parameters, except for the increase in crystallinity that occurs. This increase in crystallinity is occurring at relatively low temperatures, which,

**Figure 5** The crystallinity of mechanically processed PA material with different lengths of consolidation time at a constant temperature of 233°C.

again, indicates that large amounts of internal stored energy acting in a combined fashion with the low amounts of thermally supplied energy resulted in a solid polymer material.

The mechanical alloying technique has therefore resulted in internally storing energy within the polymer particles, which, when combined with sufficient thermal energy, results in movement or diffusion within a local region.

CONCLUSIONS

1. PA particles are continually refined with increasing mechanical milling time. Particle morphology changed from large, uneven distributed particles to small, layer structured particles. After 24 h of processing in a high-energy shaker ball mill, PA powder is quite small and the average particle size is around 3 μm .

Table VIII Strength, Ductility, and Hardness (ASTM D785) Results of Mechanically Processed PA Consolidated for Different Times at 233°C

Consolidation Time (h)	Hardness (L Scale)	Ultimate Strength (MPa)	Elongation (%)
8	86.0 \pm 0.7	105.3 \pm 1.5	23.6 \pm 0.9
14	90.0 \pm 1.0	136.4 \pm 1.2	24.3 \pm 0.8
24	93.0 \pm 0.9	141.9 \pm 1.0	24.5 \pm 0.6
36	94.0 \pm 1.0	146.1 \pm 1.2	25.0 \pm 0.8
48	94.5 \pm 1.0	146.4 \pm 0.5	24.9 \pm 0.3

2. Mechanically processed PA materials have low-temperature consolidation characteristics. The lowest consolidation temperature for mechanically processed PA powders is 100°C, which is 165°C lower than the materials' melting temperature.
3. Stronger and more ductile materials can be produced with increasing mechanical milling time. This shows that once a balance of cold welding/fracturing is reached the mechanically processed PA materials will have new optimum properties.
4. Higher consolidation temperature and longer consolidation time results in materials with higher strength, ductility, density, and crystallinity.
5. A large number of interfaces result in a higher degree of reactive surfaces. These, in turn, lead to higher bonding strength.
6. Higher activity conditions or lower activation temperatures occur due to the mechanical processing of this polymer material as a direct result of internally stored energy in the powder particles. Higher temperatures and longer consolidation times result in movement of the polymer chains.

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