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THERMAL AND MECHANICAL

ANALYSIS OF

NYLON 6 AND NYLON 6,6 BLENDS

A Thesis

Presented to

The Faculty of the Department of Chemical Engineering

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Daniel Vroom

May 1997

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ABSTRACT

THERMAL AND MECHANICAL

ANALYSIS OF

NYLON 6 AND NYLON 6,6 BLENDS

by Daniel Vroom

The properties of blends of nylon 6 with nylon 6,6 over a composition range of 5% to 50% nylon 6, have been studied by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and impact strength measurements. DSC results show increases in fusion enthalpies for the nylon 6,6 component in the blends, relative to the pure nylon 6,6 fusion enthalpy, indicating an effect on the crystallization rate by the addition of the nylon 6 component. DSC results also show the possibility of a melting point depression of the nylon 6,6 component. DMA results show smooth symmetrical damping curves for dry samples, and broad curves with shoulders on the low temperature side for samples with approximately 1 % water pick-up, suggesting a level of miscibility for the dry samples. Impact strength measurements show no gain in impact strength due to the addition of the tougher nylon 6 component, with values of the blends nearly equal to that of the nylon 6,6 component.

ACKNOWLEDGMENTS

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CHAPTER 1
INTRODUCTION AND BACKGROUND

1.1 INTRODUCTION

Since the first synthetic plastics were developed in the 1930's, the plastics industry

has experienced tremendous growth. From the period of 1970 to 1986, consumption of

plastics has increased from 20 billion to 50 billion pounds per year (1). This growth has

resulted from plastics being able to replace existing materials, such as metals, glasses, and

ceramics in certain applications (1). Their relatively low densities and range of

mechanical properties afford them many possible uses. The blending of existing plastics

to tailor specific properties, as opposed to the development of new polymers, has been

of special interest, due to lower costs. A class of plastics known as nylons have been

particularly important in the industry due to their properties. The blending of two nylons,

nylon 6,6 and nylon 6, is investigated in this thesis.

1.2 HISTORY AND PROPERTIES OF NYLONS

Nylons are a class of polymers known as polyamides. Prepared by the condensation

reaction of diamines and dibasic acids, nylons were first synthesized by Carothers at du

Pont in the mid 1930's (2). Since that time, they have become one of the most

technically and commercially important polymers. Nylons are manufactured to produce

both fibers and molded plastics, representing about twenty-five percent of all fibers and

about forty percent of all molded plastics produced nationally. The annual growth of the

nylon industry is estimated at nearly ten percent per year (2).

Molded nylon plastics have many important industrial uses. Applications include automobile and aircraft parts, gears and bearings, appliances and power tools, and electrical and electronics components (3). Their strength, relatively high melting points (220-300 C), and light weight (compared to metallic materials), make nylons attractive for these types of applications, and insures future research into new applications.

Nylon 6,6 is prepared by the reaction of hexamethylene diamine with adipic acid at about 280 C, while nylon 6 is prepared by the ring-opening polymerization of caprolactam. The chemical repeat unit of both polymers is shown in equations [1] and [2].

$$\text{Nylon 6} \qquad -[\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}(CH_2)_5NH]- \qquad\qquad [1]$$

$$\text{Nylon 6,6} \qquad -[NH(CH_2)_6NH\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}(CH_2)_4\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}]- \qquad [2]$$
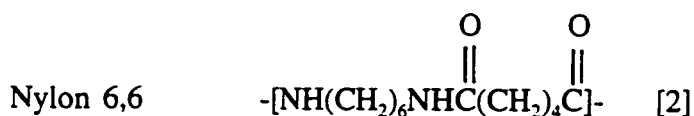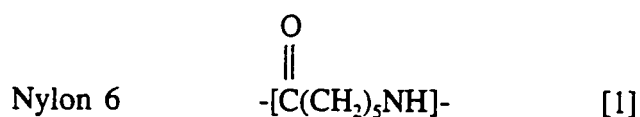
Molecular weights typically range from about 2,000 to 50,000 g/mol (3).

Although nylons do not achieve high molecular weights in comparison to certain vinyl polymers which may have molecular weights greater than 100,000 g/mol, they do form products with strong mechanical properties. This is due in large part to the significant degrees of crystallinity (up to 50%) that nylons can achieve (4). Nylons form linear polymers, that undergo intramolecular hydrogen bonding, leading to their high

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crystallinities at relatively low molecular weights. At a molecular weight of about 2000 g/mol for instance, nylon 6,6 will be a hard brittle solid while polyethylene will be a waxy solid. This is due to the fact that the only intramolecular forces between the polyethylene molecules are van der Waals forces, which only become significant at very high molecular weights (>100,000 g/mol) (3).

Nylons form products that have high tensile and compressive strengths, however their impact strengths may be less than what is needed for certain applications. They are also notch sensitive, which can lead to failure at the site of nicks, scratches, or chemical degradation (4). These properties are due to the high degrees of crystallinity. For this reason, nylons often have to be modified in some manner, such as reinforced, plasticized, or blended, in order to produce parts of suitable impact strength (4).

1.3 IMPORTANCE OF POLYMER BLENDS

The blending of polymers has steadily increased in scope and importance in the last several decades (3). The mixing of two or more polymers, which have different properties, to give a product with some desirable intermediate property, is not only a technically sound practice but usually less costly and time consuming than synthesizing a new polymer (3).

Some of the benefits of poly-blending include enhanced processability, increased modulus for elastomers, decreased modulus for thermoplastics, improved thermal properties, and improvement in impact resistance (3). By blending polymers in certain

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compositions, one can tailor the end product to meet the end needs, in terms of mechanical and thermal properties.

Polymer blends also can have advantages over other types of polymer modifiers, such as small molecule plasticizers. Many brittle plastics, such as polyvinyl chloride (PVC), often have to be plasticized to prevent cracking and enhance processability. Addition of small molecule modifiers (plasticization) can decrease the modulus enough to prevent brittleness. However, the plasticizer may be leached or vaporized out of the polymer due to contact with certain solvents or excessive heat. This can again lead to brittleness and cracking. If a brittle polymer can be plasticized with another compatible polymer, however, this problem can be avoided.

1.4 SELECTION OF BLEND COMPONENTS

For a blend of two polymers to be miscible, the excess Gibbs energy must be negative. The expression for the free energy for a mixture (where the subscript m denotes mixture, is given by equation [3].

$$\Delta G_m = \Delta H_m - T \Delta S_m \quad [3].$$

For a two polymer system, the change in entropy ΔS, while positive, is usually very small due to the fact that the system contains relatively few large molecules, resulting in relatively few possible configurations. Thus, for most polymer blend systems, the free energy is basically a function of the heat of mixing, which must be near zero or negative for spontaneous mixing but is usually positive for polymer/polymer systems.

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Equation [4] by Hildebrand and Scott (3) is a widely used equation for calculating ΔH.

$$\Delta H_m = V_m[(\delta_1 - \delta_2)^2]\, \phi_1\, \phi_2 \quad [4]$$

where V_m is total volume of the mixture, δ is the solubility parameter and ϕ is the molar volume of the components. Inspection of equation [4] reveals that it will only calculate positive values for the heat of mixing. Thus, according to [4], all polymer blends will exhibit phase separation. However, miscible systems have been identified. The discrepancy arises from the fact that equation [4] does not take into account possible strong interactions between molecules such as dipole/dipole interactions or hydrogen bonding. Such strong interactions between molecules can lead to negative values for the heat of mixing and thus miscibility. This suggests that selecting a polymer system in which strong interactions between the polymer chains can occur can possibly lead to miscibility.

The selection of which polymers to blend is also a function of the properties that are needed for the end product. The most common blends involve those between elastomers and plastics, two amorphous plastics, crystalline and amorphous plastics, and less commonly two crystalline plastics. In many instances, plastics can be too brittle for many applications. The addition of an elastomer can increase the impact strength to acceptable levels. Conversely, the addition of a rigid plastic to an elastomer can increase the modulus of the elastomer.

The change in properties of the major component polymer by the addition of the

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minor component polymer is partly a function of the amount of minor component added. It is also a function of how well phases adhere to each other in immiscible systems. By measuring the desired property as a function of blend composition, one can determine the optimum composition to achieve the desired results.

As previously discussed, the compatibility of the selected polymers is a major concern. Most polymers tend to be thermodynamically incompatible, leading to some degree of phase separation. If the polymer pair is totally immiscible, mechanical properties can suffer if there is poor adhesion at phase boundaries. For example, fractures can initiate at poorly joined phase boundaries. However, partially compatible, or less commonly, totally compatible pairs, can lead to significant improvements in properties. The better adhesion at phase boundaries, in partially miscible blends for example, can give rise to better mechanical performance.

1.5 ANALYSIS OF BLEND PERFORMANCE

In analyzing the blends of two polymers, the level of compatibility of the blend and the resulting effects on the physical properties are of interest. The major physical parameter in determining miscibility is the glass transition temperature. A totally immiscible system will exhibit two distinct glass transitions, while a miscible pair will exhibit a single glass transition that is usually the weight average of the pure component transitions (2).

The analysis of mechanical properties is also important in the analysis of blends. In

general, two component mixtures may be described by equation [5].

$$P = P_1C_1 + P_2C_2 + IP_1P_2 \qquad [5]$$

where P is a particular property of the blend, C is the concentration (subscripts denote component 1 and 2 respectively), and I is an interaction parameter which describes the thermodynamic compatibility of the two components (2). When I is greater than zero, the blend is termed synergistic and has property values better than those that would be calculated from the weighted average. Conversely, I values less than zero are termed nonsynergistic, and have property values less the weighted averages. When I equals zero, property values reflect the weighted averages. This behavior is illustrated in Figure 1.

Miscible or partially miscible blends tend to display synergistic or non-synergistic behavior over the entire composition range. Synergistic behavior may arise from molecular interactions between chains, while non-synergistic behavior can be caused when a molecular interaction is disrupted due to the addition of a second polymer (2). Immiscible blends will usually exhibit synergistic behavior over part of the composition range, and non-synergistic behavior over the rest, depending on which component is the continuous phase (5).
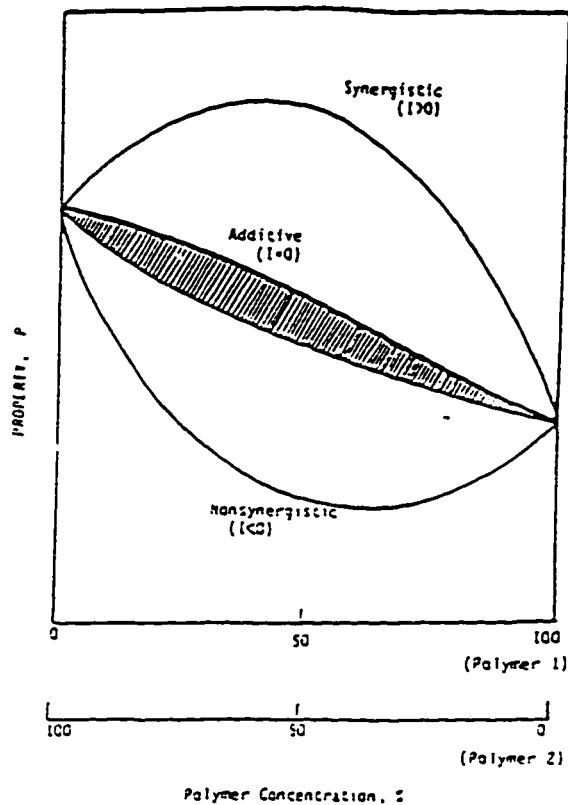
Figure 1: Property relationship versus blend concentration.(3)

1.6 SCOPE OF STUDY

This study investigates the effects of blending two semi-crystalline polyamides, nylon
6.6 as the major component (except for the 50% blend), and nylon 6 as the minor
component, and attempt to determine the compatibility of the blend and the resulting
effects on the thermal and mechanical properties. This was done using thermal analysis
(DSC) , dynamic mechanical analysis (DMA), and the measurement of Izod impact
strength of various blends.

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CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

While many investigations have been done in the field of polymer blends, considerably less has been undertaken in the area of nylon/nylon blends. The trend towards finding compatible polymer pairs has been of particular interest. The ability to predict miscibility in blends, either through the development of semi-empirical relations, or the modification of expressions describing the thermodynamics of mixing for polymer systems has also been of interest.

2.2 ANALYSIS OF BLENDS

The analysis of blends is principally concerned with determining phase behavior of the components. The presence of a single glass transition (Tg) is generally the main determinant of miscibility. Different methods, some more sensitive than others, are often employed to determine Tg's of mixtures. In an early work on the miscibility problem, Sperling et al. (6) investigated the system polyethyl acrylate (PEA) and polymethlymethacrylae (PMMA). Dilatometric measurements indicated the presence of a single Tg. The authors presented several possible interpretations for this result. Most notably, that the single Tg was due to a miscible system. However the authors also surmised that the transitions of each component may have been "run together" due to

pressure caused by unequal expansion coefficients. Their ultimate conclusion was that more sensitive measurements were needed to clarify the situation.

Calorimetric and dynamic mechanical measurements, have proved to be more sensitive in Tg determinations. Bernstein, et al. (7) studied the blends of polyvinylidene flouride (PVF) with polyvinyl acetate (PVAc), polyvinyl propionate (PVPr), and polyvinyl butyrate (PVBu). Samples of blends were subjected to differential thermal analysis (DTA) and dynamic mechanical measurements (DMA). The systems PVF/PVPr and PVF/PVBu exhibited two alpha peaks on damping curves (loss modulus versus temperature) indicating two glass transitions, therefore immiscibility. The system PVF/PVAc, however, exhibited only a single alpha peak over the entire blend composition range. Furthermore, the crystallization of PVF is affected by the addition of PVAc. DTA results indicated that PVAc depressed the melting point of PVF, suggesting that PVAc is a miscible diluent for PVF.

DSC and DMA studies were used by Schurer (8) to investigate isotactic (i-) and syndiotactic (s-) forms of PMMA blended with polyvinyl chloride (PVC). DSC scans for the i-PMMA/PVC system indicate two distinct endothermic shifts in the baseline, indicating two phases. DMA damping curves confirm this result, showing two loss maxima. The system s-PMMA/PVC shows only a single damping maxima for all compositions indicating miscibility.

MacKnight, et al. (9) studied the system poly(2,6-dimethylphenylene oxide) (PPO)/polystyrene (PS). A single glass transition between the two single component

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transitions indicated miscibility. However, DMA measurements, showed a loss maxima that was at least partially resolvable into two peaks. This would indicate that DMA is somewhat more sensitive than DSC for determining multiple glass transitions. Dielectric relaxation measurements on this system revealed only a single, somewhat broadened maximum for the mixtures. The authors conclusions were that mixing did not occur at the segmental level, but mixing did occur to an extent between pure polymer rich phases such that distinct Tg's were not observed, although broadened ones were.

Since the glass transition is characterized by a sharp decrease in elastic modulus, it seems reasonable to expect that mechanical measurements would be more sensitive to this "mechanical event" than thermal measurements would. DSC may not be sensitive enough for determining transitions in blends in which the pure component Tg's are as close as in the MacKnight study (9).

2.3 MISCIBILITY AND MECHANICAL PROPERTIES

The miscibility of a polymer system usually has a strong influence on the mechanical properties. Yee (10), studied blends of poly(2,6-dimethyl p-phenylene oxide) (PM2PO) and polystrene (PS). DSC and DMA measurements indicated a single Tg over the entire composition range, which lead to the conclusion of miscibility. Tensile stress measurements of each blend showed positive blending effects, with a maxima at the 10% mixture. The author thus concluded that mixing had occurred on a segmental level.

Blending can have negative effects on mechanical properties as well as positive

effects. Mekhilef, et al. (11) investigated the behavior of polystyrene (PS) blended with styrene-isoprene-styrene (SIS) and ethylene-propylene rubber (EPR). The Izod impact strength of the PS/EPR system and the PS/SIS system both showed negative blending effects up to 20% modifier. SEM analysis showed voids and sharp boundaries around the EPR rich phases (PS/EPR blend) resulting in a weak interphase and the resulting poor impact strength. The PS/SIS system showed a similar weak interphase.

Chin and Hwang (12) investigated the additions of polycarbonate (PC) and nylon 6 (PA 6) to ABS rubber. Blends of ABS 1000/PC and ABS3000/PC showed negative blending effects for notched Izod impact tests over the entire composition range as illustrated in Figure 2. However, tensile modulus measurements for the same system showed negative effects only below about 50%, with positive blending effects above this value. This behavior can be seen in Figure 3.
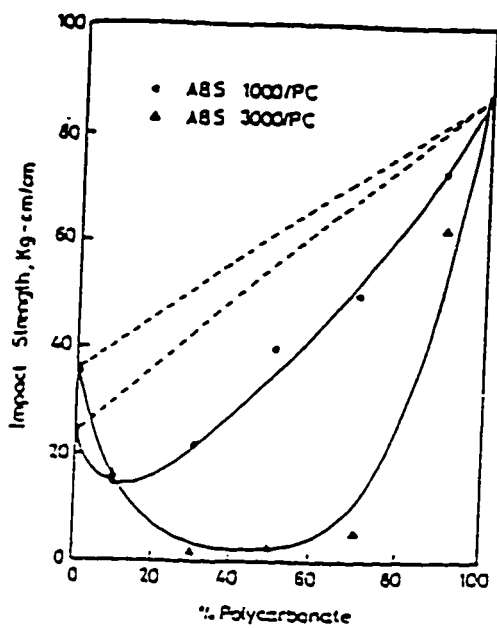
Figure 2. Notched Izod impact strength versus composition. (12)
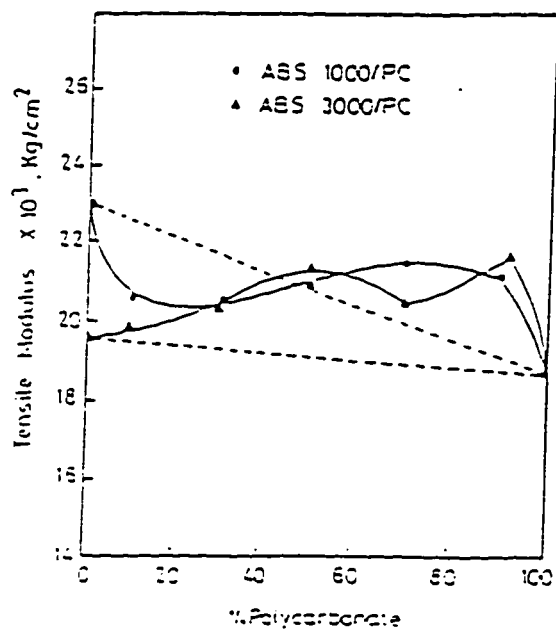
Figure 3. Tensile modulus versus composition. (12)

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2.4 NYLON 6 / NYLON 6,6 BLENDS

Relatively few studies have been done in the area of nylon/nylon blends. This may be due to the fact that when one or both polymers are able to crystallize, the result is usually immiscibility (13). Three studies of nylon/nylon blends have been found. In one study, mixing was accomplished through the melting of discs of each polymer during heating in a DSC. In a second study blends were prepared by coprecipitation from a common solvent. A third study, examined blends of PA 6 and PA 6,6 processed as drawn fibers.

Rybnikar and Geil (14) studied the crystallization and melting behavior of contact laminates. DSC scans of the laminates revealed melting endotherms for both polymers for PA 6 percentages from 15.5 to 90.8. Percent crystallinities of each, as determined from the heats of fusion, were very close for each (around 15 %) over the entire composition range. Blending also lowered the melting points of each (about 15 C for PA6 and about 10 C for PA 6,6). Although the authors did not examine the Tg's of the blends, they did conclude that the blend was at least partially soluble in the melt due to the melting and crystallization behavior.

Ellis (15), examined solution precipitated blends of various aliphatic polyamides, including the PA 6/ PA 6,6 blend. DSC thermograms and enthalpy recovery measurements suggested phase separation for most blends. However results were inconclusive for the PA 6/ PA 6,6 blend. While DSC scans were inconclusive, enthalpy recovery suggested to the author at least partial miscibility.

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Verma, et al. (16) investigated PA 6/ PA 6,6 blends in the form of extruded filaments, both drawn and undrawn. Crystallinity of both components was determined by DSC from 30% to 80% PA 6. DMA behavior of the filaments showed only single peaks for the blends on plots of tan delta versus temperature. This suggested to the authors compatibility in the amorphous regions. The filaments also exhibited higher modulus and tenacity as compared to the pure polymers.

These three studies suggest the possibility of miscibility for PA6/ PA 6,6 blends. However, the different preparation of each blend did produce variations in the crystallinities of each blend. Melt blended, molded plastics, may show significant differences in morphology than in filaments and drawn fibers, the processing of which usually increases orientation.

CHAPTER 3

EXPERIMENTAL

3.1 INTRODUCTION

The method of investigation consisted of preparing samples of various compositions and analysis by thermal, dynamic mechanical, and impact strength measurements. Thermal measurements were made by differential scanning calorimetry (DSC) and determined heats of fusion, degrees of crystallinity, and melting points of one or both polymers. Dynamic mechanical measurements where used to determine the behavior of the blends in the amorphous phase. Finally, the results of blending on the impact strength were investigated by Izod impact measurements.

3.2 MATERIALS

The nylon 6,6 used in all blends was supplied by Du Pont as ZYTEL 101 and had a molecular weight of 50,000 g/mol relative to polystyrene calibration as determined by gel permeation chromatography. Nylon 6 was supplied by BASF under the trade name UTRAMID B and also had a molecular weight of 50,000 g/mol relative to polystyrene calibration. High density polyethylene, supplied by Dow Chemical, was used as a purging compound during injection molding operations.

3.3 SAMPLE PREPARATION

3.3.1 COMPOUNDING

The first step in sample preparation was mixing of the polymers. The nylon 6,6 and nylon 6 resins were dried for four hours at 80 C and then melt blended in a twin screw extruder and re-pelletized. Compositions for each blend are listed in Table 1. Pure components were not extruded and re-pelletized.

Table 1. Sample blend compositions.

Sample	% PA 6	%PA 6,6
1	0	100
2	5	95
3	10	90
4	20	80
5	35	65
6	50	50
7	100	0

3.3.2 INJECTION MOLDING

In any molding process involving nylons, thorough drying of the resin is critical. At equilibrium with 50 % relative humidity, nylon 6 will have a mean moisture content

of 2.7 % by weight, and nylon 6 a 2.5% by weight moisture content (5). Whelan (18) recommends a moisture content of < 0.2 % to avoid such problems as hydrolysis during processing (17). All resin prior to molding was therefore dried under vacuum at 75 C for a period of 24 hours. Moisture analysis of a sample of the 10% blend (titration with Karl Fisher reagent) indicated a moisture content of 0.19%.

The resin was immediately molded after drying to prevent any possible moisture pick up. Molding was done on a Gluco P60 injection molder producing bars with lengths of 4.8", widths of 0.5", and thicknesses of 0.31". Samples for each of the individual tests were then cut or machined from these bars.

3.3.3 PREPARING SAMPLES FOR INDIVIDUAL TESTS

For DSC analysis, samples were cut into weights recommended by ASTM D 3417-83. Cross-sectional cuts of 4/100 inch were cut from the injection molded bars. These thin sections were then cut down to give a flat sample with a weight of 5 to 10 mg.

For DMA analysis, samples were machined from the molded bars to give specimens with lengths of 40 mm, widths of 12 mm, and thicknesses of 3 mm.

For impact strength tests, the original bars, which had a thickness of .31" were machined down on both sides to give a final thickness of 1/4". The bars were then cut into lengths of 2 3/8", to give specimens with the dimensions 2 3/8" x 1/2" x 1/4". These specimens were then notched according to ASTM D 236.

All cut samples were double wrapped in airtight plastic to minimize moisture pick up.

Thus in accordance with ASTM standards D 256, D 3417, and D 4065, for hygroscopic materials, all samples were tested dry as molded.

3.4 SAMPLE ANALYSIS

3.4.1 DSC ANALYSIS

In differential scanning calorimetry, a sample and reference are simultaneously heated and the energy required to keep both at the same temperature (d_bQ/dt) is recorded. The change in energy required for this is directly related to thermal transitions in the sample. A typical semi-crystalline polymer DSC thermogram is illustrated in Figure 4.
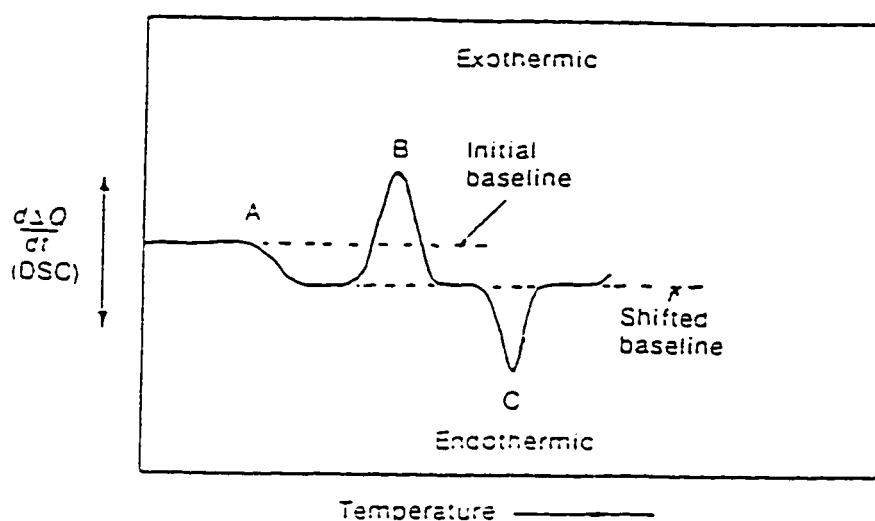
Figure 4. Idealized DSC thermogram (3).

Point A represents the glass transition, point B is a crystallization or recrystallization exotherm, and point C is the crystalline melting point, Tm, with the corresponding heat of fusion peak.

All DSC experiments were preformed on a System 7 Perkin-Elmer Differential Scanning Calorimeter. The instrument was calibrated using a two point calibration with indium and zinc standards according to the manufacturer's instructions. The data for the calibration is tabulated in Appendix 3.

For nylon samples, 5 to 10 mg. disks were weighed to the nearest 0.1 mg and then enclosed in a covered sample pan. All samples were scanned from 50 C to 300 C at a heating rate of 10 C per minute.

The data obtained from the DSC thermograms, from the thermal transitions, included the melting points of either blend component (taken as the peak maximum of endotherms) along with the fusion enthalpies associated with each. The fusion enthalpies were then used to estimate the degree of crystallinity of either component.

3.4.2 DYNAMIC MECHANICAL ANALYSIS

Dynamic mechanical analysis (DMA) is a technique in which the dynamic mechanical moduli, E' and E", of a sample are measured as functions of time , frequency, and temperature. The quantity E' is the storage modulus and is a measure of the energy which is stored elastically when a sample is subjected to repeated cycles of deformation. The quantity E" is the loss modulus and is a measure of the energy which is dissipated

through friction. Another quantity in common use is the loss tangent, tan δ, which is the ratio of the loss modulus to the elastic modulus, with δ the angle between the in phase and out of phase components of the cyclic deformation.

By following the elastic and loss modulus and tan delta as a function of temperature for a fixed frequency, transitions in samples can be determined. At the glass transition, for example, a sample experiences a significant decrease in modulus. A plot therefore of the elastic modulus, E', against temperature will show a sharp decrease at the glass transition. Plots of the loss modulus, E", or tan delta, however, will show maxima at the glass transition. These behaviors are illustrated in Figure 5.
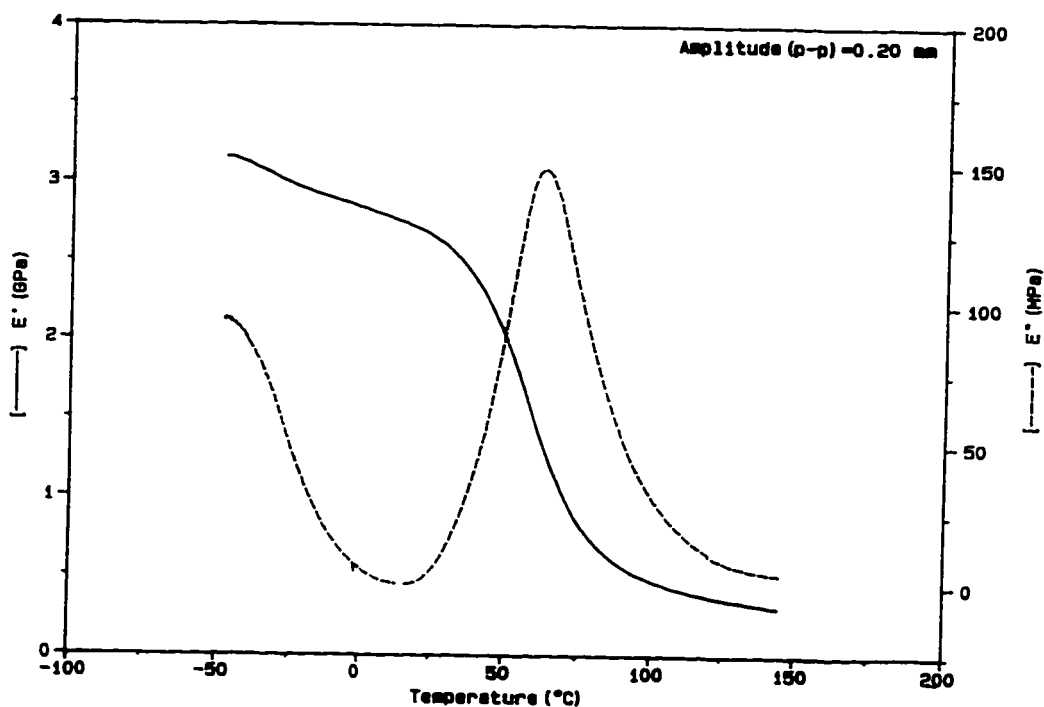
Figure 5. Idealized dynamic mechanical spectroscopy.

For the purposes of this study, DMA was used to determine phase behavior in the amorphous regions of the blends. A miscible blend will exhibit a single glass transition somewhere between the values for each of the pure components. An immiscible blend, however, will exhibit two glass transitions, which is indicative of some degree of phase separation in the amorphous region.

All dynamic mechanical experiments were preformed on a Du Pont 983 Dynamic Mechanical Analyzer (DMA). The instrument was operated in " Resonance mode " which consisted of running samples at the resonant frequency (16-17 Hz.) of a compound system which consisted of the sample and sample holder. Plots of elastic and loss modulus versus temperature were produced for each sample for the purpose of determining transitions in the polymer. Measurements covered the temperature range of -5 C to 150 C.

3.4.3 IMPACT RESISTANCE MEASUREMENTS

Impact resistance is a measure of a materials ability to withstand sudden loads. The ability of a material to withstand a sudden load without failing, depends on its properties. Polymers which crystallize will usually have larger tensile and compressive strengths than elastomers; however, they will usually have lower impact strengths. Improving the impact resistance of the more brittle plastics is one of the main reasons for blending polymers.

The improvement of mechanical properties in many instances depends on how well

the polymers mix. Poor adhesion at phase boundaries can lead to failure at those points. When polymers exhibit some degree of mixing, mechanical properties generally tend to improve. For instance, in partially miscible blends, partial mixing at phase boundaries can help hold the entire sample together when sudden loads are applied.

In this study, blend samples were subjected to impact resistance measurements, to determine the effects of blending on the impact strength and whether these results can lead to any conclusions on the miscibility of the blends.

Ten samples of each composition were prepared, machined and notched as previously described. Measurements were made on a Baldwin Universal Impact Tester. Values of the breaking energy, measured in ft-lbf per inch of notch, were determined for each blend and pure component.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 INTRODUCTION

Results consist of data obtained from DSC analysis, DMA spectroscopy, and Izod impact strength measurements. DSC analysis consisted of determining the behavior of the blends with respect to fusion enthalpies of one or both polymers, and their respective melting points. DMA, on the other hand, was used to determine behavior in the amorphous regions of the polymer. Finally, measurements of the Izod impact strength were made for each sample to determine the effects of the various blend compositions on this property.

4.2 DSC ANALYSIS

4.2.1 MELTING BEHAVIOR

The melting behavior of the pure samples is shown in Figure 6. The values of the melting points (taken as the peak maximum), 219.2 C for nylon 6 and 261.1 C for nylon 6,6 were in good agreement with the literature, 220 C and 255 C (17), respectively. Figure 6 reveals two distinct features in the melting of nylons. First, both pure samples melt over a rather broad temperature range of 10 to 20 C, as opposed to the nearly isothermal melting of non-polymeric crystalline solids. This is not unusual for polymers and is attributed to crystal imperfection resulting from poor chain alignment (2).

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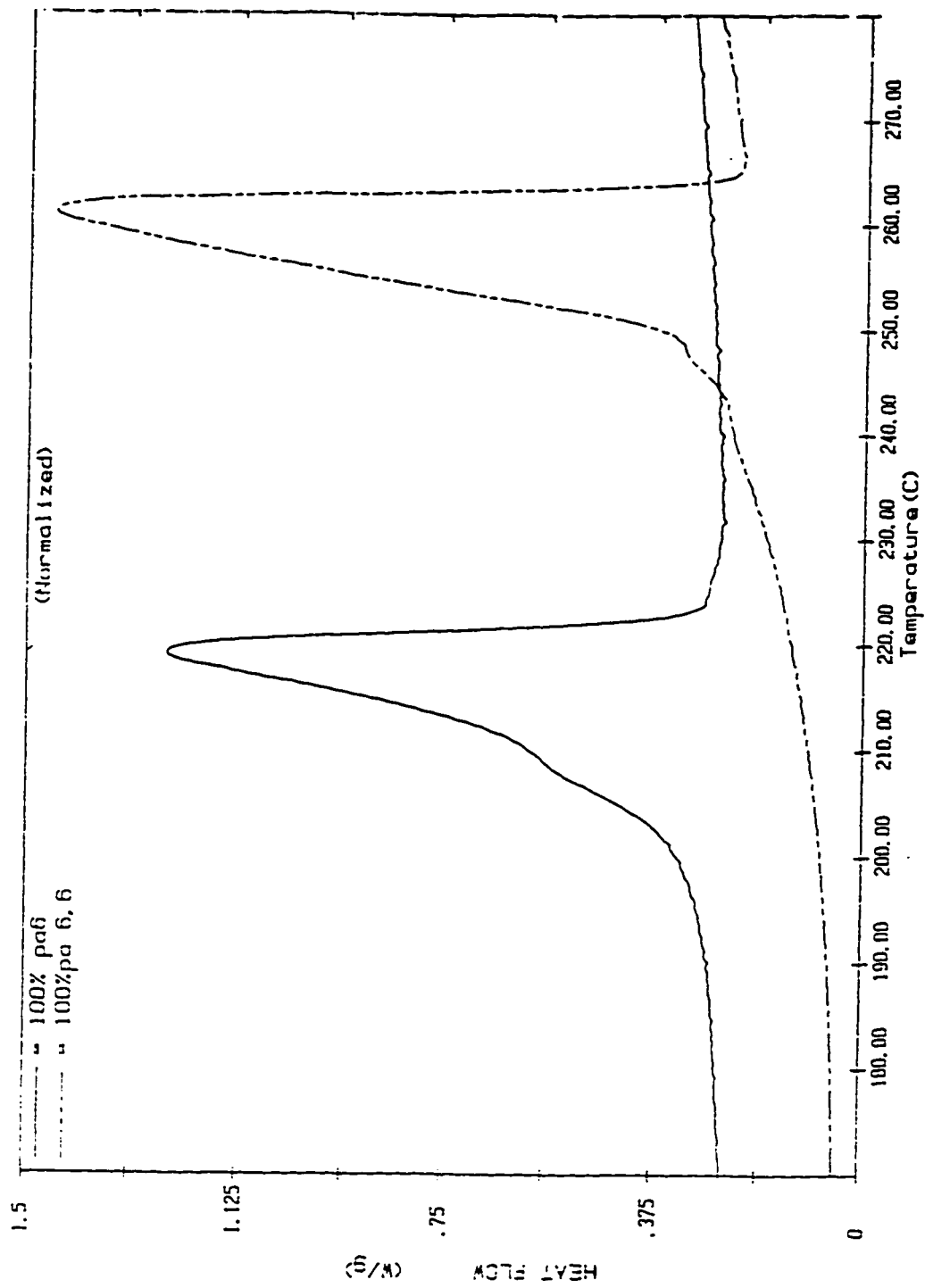
Figure 6. Melting behavior of pure samples.

Also evident from Figure 6 are shoulders on the low temperature side of the endotherms. This has also been attributed to the melting of imperfect crystals. As the crystal structure becomes more imperfect, the melting point will usually decrease (5). Depending on the cooling rate from the melt, and the heating rate in DSC analysis, this shoulder will either disappear or turn into a small peak.

Sweet and Bell (19) studied this behavior for nylons and determined that this was attributed to lower energy crystals melting followed by the melting of the higher energy crystals in the large endotherm. If the heating rate is low enough, these lower energy crystals may melt, recrystallize and then melt again. Figure 6, however, does not indicate any exothermic behavior, thus no significant recrystallization was determined to occur at the heating rate (10 C/min.) employed in the DSC experiments.

The melting behavior of each of the blends is illustrated in Figure 7. Each of the blends show melting peaks for the nylon 6,6 component, while only the 50% and 35% blends show a melting peak for the nylon 6 fraction of the blend. Notable is the broadness of the nylon 6 peaks in comparison to the nylon 6,6 peaks. This is most likely due to the nylon 6,6 crystallites forming first on cooling from the melt. The forming of nylon 6,6 crystals along with the increasing rigidity of the nylon 6,6 amorphous material with decreasing temperature would severely limit the ability of the nylon 6 chains to align to any large degree. Nylon 6 repeat units also have no center of symmetry, as do the nylon 6,6 repeat units. The nylon 6 chains, therefore, would need a common alignment for the formation of hydrogen bonds in crystals. Molecules that were aligned in opposite

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directions would not have the required alignment of hydrogen bonds. These factors would most likely result in nylon 6 forming small, imperfect crystals which would melt at lower temperatures and over a broader temperature range.
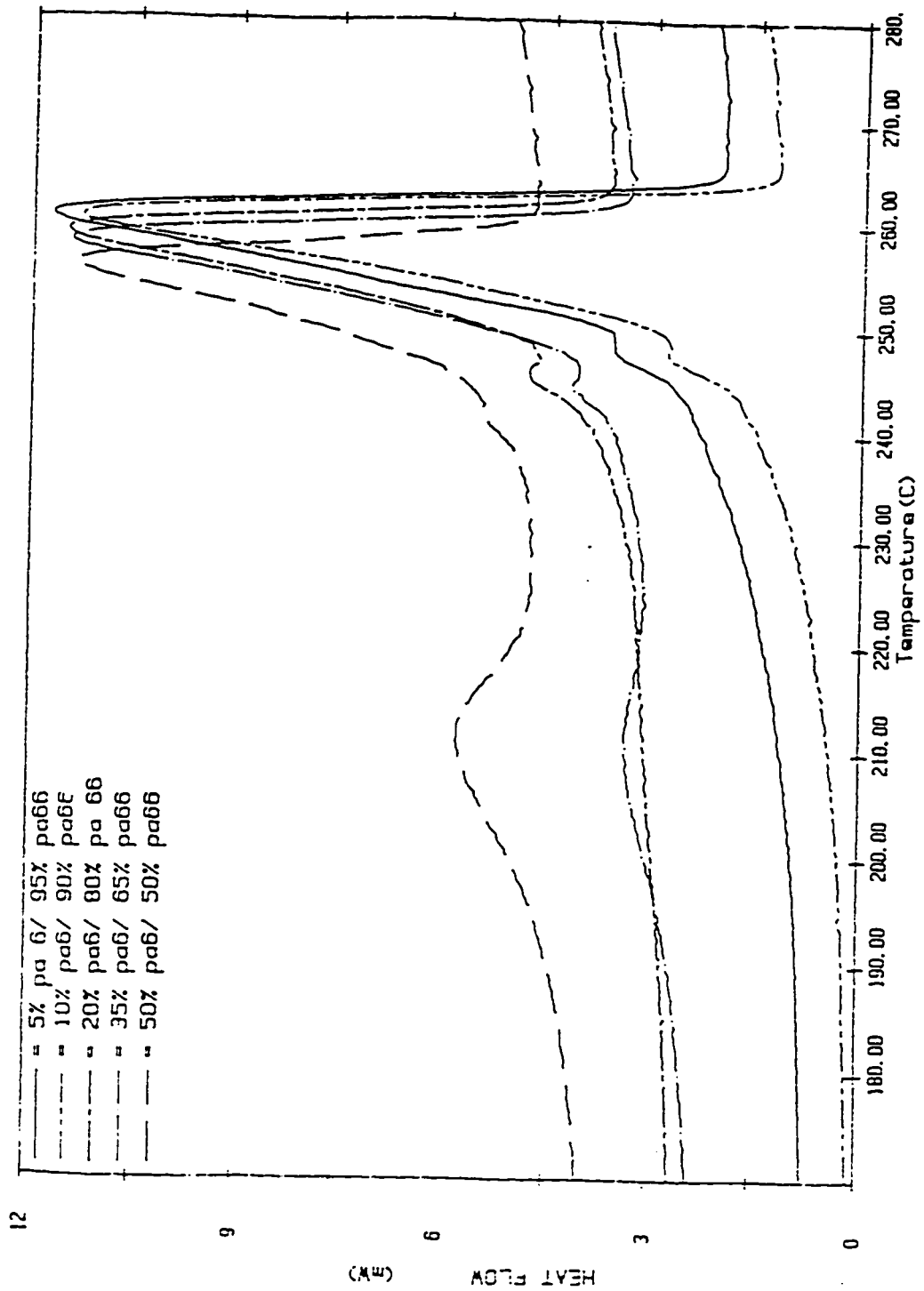
Figure 7. Melting behavior of blend samples.

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As shown in Figure 7, the peak melting temperature of the nylon 6 component is 211.3

C for the 50% blend and 208.6 C for the 35% blend as compared to a value of 219.2 C

for the pure nylon 6 sample.

The nylon 6,6 melting endotherms, however, do not significantly broaden or change

shape over the entire composition range. Comparison of the nylon 6,6 peak in Figure 6

with the nylon 6,6 peaks in Figure 7 shows similar peaks in terms of shape, although the

maxima of the peaks decreases by about 5 C from 0% to 50% nylon 6 content. The

similarity of the endotherms would not be unexpected due to nylon 6,6 being the major

component in all blends (except the 50% blend) and also because the nylon 6,6

component will crystallize first in blends where both components crystallize. The

significance of the decrease in peak melting temperature will be discussed in the

following section.

The heats of fusion for each sample were determined from integration of the

endotherm peaks. The values for the normalized heats of fusion are summarized in Table

2.

Table 2. Normalized fusion enthalpies.

% PA 6	Hf1 (J/g ± 0.1)	Hf2 (J/g ± 0.1)
0	---	67.9
5	---	68.3
10	---	66.5
20	---	70.7
35	18.0	73.8
50	28.0	77.9
100	57.7	---

The fusion enthalpies of the pure components, 57.7 J/g for nylon 6 and 67.9 J/g for nylon 6,6 are typical values for melt crystallized nylons (6). As shown in Table 2, the heat of fusion for the nylon 6,6 component in the blends shows a somewhat unusual behavior. With the exception of the 10% blend, which has a fusion enthalpy of about 2% less than the pure component, the fusion enthalpies steadily increase with increasing nylon 6 content. Although unusual, this behavior has been seen in other polymer systems (7). The addition of a diluent to a crystalline polymer, whether polymeric or small molecule, will usually inhibit the crystallization rate and thus the degree of crystallinity.

The increase of the fusion enthalpy of the nylon 6,6 component with increasing nylon 6 content may indicate that the nylon 6,6 and nylon 6 chains may be interacting to some

extent on a molecular level. The 50% blend, for example has a nylon 6,6 fusion enthalpy of 77.9 J/g while the pure 6,6 component has a fusion enthalpy of only 67.9 J/g, even though it contains twice as much nylon 6,6 as the 50% sample. Each component forms crystals from hydrogen bonded sheets of folded chains (6), in which the hydrogen bonds are perfectly formed; thus it is not believed that any cocrystallization occurs. Therefore to see increases in fusion enthalpy of the 6,6 component, there likely may be some interactions between segments of nylon 6 chains and nylon 6,6 chains in the melt. Nylon melts have relatively low entropies due to significant degrees of hydrogen bonding. Water has been shown to disrupt this effect in the melt, leading to a decrease in viscosity (4). This allows the chains greater mobility and thus increases the crystallization rate (4). The addition of the nylon 6 chains in the blends may have the same effect of disrupting the hydrogen bonds, although the decrease in viscosity would be somewhat offset by the high molecular weight nylon 6 chains. This may also lead to a higher crystallization rate for some of the blends, and the subsequent increases in the nylon 6,6 fusion enthalpies for the blends.

Although the fusion enthalpy of the nylon 6,6 component in the blend increases over the composition range, the total crystallinity of the sample (nylon 6 + nylon 6,6) based on the weight percent of the components, decreases from 34.6 % for the pure nylon 6,6 sample to 27.3 % for the 50 % blend. Results for the remaining samples are tabulated in Appendix B.

4.2.2 MELTING POINT BEHAVIOR

The melting points of the nylon 6,6 and nylon 6 components of each blend as a function of composition are summarized in Table 3.

Table 3. Peak melting temperature versus composition.

% PA 6	Tm_1 (C ± 0.1)	Tm_2 (C ± 0.1)
0	---	261.1
5	---	261.2
10	---	261.0
20	---	259.6
35	209.9	258.7
50	211.3	256.4
100	219.2	---

Subscript 1 refers to nylon 6 and subscript 2 refers to nylon 6,6.

The melting point of the nylon 6,6 component is virtually the same for the 0%, 5%, and 10% nylon 6 compositions, then begins to drop by about a degree for the 20%, 35%, and 50% nylon 6 compositions. The question arises as to whether this is due to a morphological effect in which poorer quality crystals are formed with increasing nylon

6 content, or whether the lowering of the melting point is a true thermodynamic depression caused by an increase in the entropy due to the presence of a miscible diluent (nylon 6 chains).

Equation [6] (19) represents the melting point depression of a crystalline polymer by the addition of an amorphous polymer.

$$\frac{1}{Tm} - \frac{1}{Tm^\circ} = \frac{R\ V_{2u}}{H_{2u}\ V_{1u}} \ X_{12}\ (1-V_2)^2 \qquad \text{Eq. [6]}$$

where,

Tm° = equilibrium melting point

Tm = melting point in mixture

V_u = molar volume of repeat units

V_2 = volume fraction

H_{2u} = enthalpy of fusion per mole of repeat unit

X_{12} = Flory interaction parameter

R = gas constant

and where subscript 1 refers to the amorphous polymer and subscript 2 the crystalline polymer. Observation of Equation [6] reveals that a melting point depression will only occur for negative values of the interaction parameter, X_{12}. Applying this equation to the nylon 6 / nylon 6,6 blend system and assuming that the nylon 6 component behaves as

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an amorphous polymer in the 10, 20 , and 35 % blends (due to no or very little observed

nylon 6 crystallization in these blends) the melting point depression as a function X_{12} can

be determined. Table 4 summarizes the results for the 10, 20, and 35 % blends. A value

of X_{12} of about -0.3 would represent a system of total compatibility, and the value of X_{12}

of -0.01 would be representative of a partially miscible system (19).

Table 4. Tm versus X_{12}.

	Tm		
X_{12}	10%	20%	35%
-0.3	260.84	259.94	256.90
-0.2	260.92	260.32	258.29
-0.01	261.09	261.06	260.96

Comparing the values in Table 4 with the melting point of the pure polymer, 261.1 C,

very little depression in melting point is observed. The largest drop is only about 4 C for

the 35% blend at a value of X_{12} of -0.3 which represents a totally miscible system. The

values for the calculated melting point depressions are however, similar to the actual

measured values (Table 3), indicating the possibility of a thermodynamic melting point

depression. However, the small temperature drop is also on the order of what might be

expected if poorer quality crystals were formed. Studies of isothermally crystallized

samples may provide more insight into which phenomena is causing the lowering of the

melting point of the nylon 6,6 component.

4.3 DMA ANALYSIS

4.3.1 DAMPING BEHAVIOR

The damping behavior of the nylon 6 and nylon 6,6 pure samples is shown in Figure 8, which plots the loss modulus, E", as a function of temperature. Taking the glass transition as the maximum of the loss peak, values of 63.4 C for nylon 6 and 77.9 C for nylon 6,6 were determined. Nylon 6 also displays a higher value for maximum damping, 185 MPa to 145 MPa for nylon 6,6. As would be expected for pure samples, both curves are fairly symmetrical with no evidence of shoulders on either. However, the transitions of both samples are rather close, a 14.5 C difference. This would tend to make determinations of phase behavior in the amorphous regions rather difficult as compared to samples whose transitions are separated by fifty or more degrees.
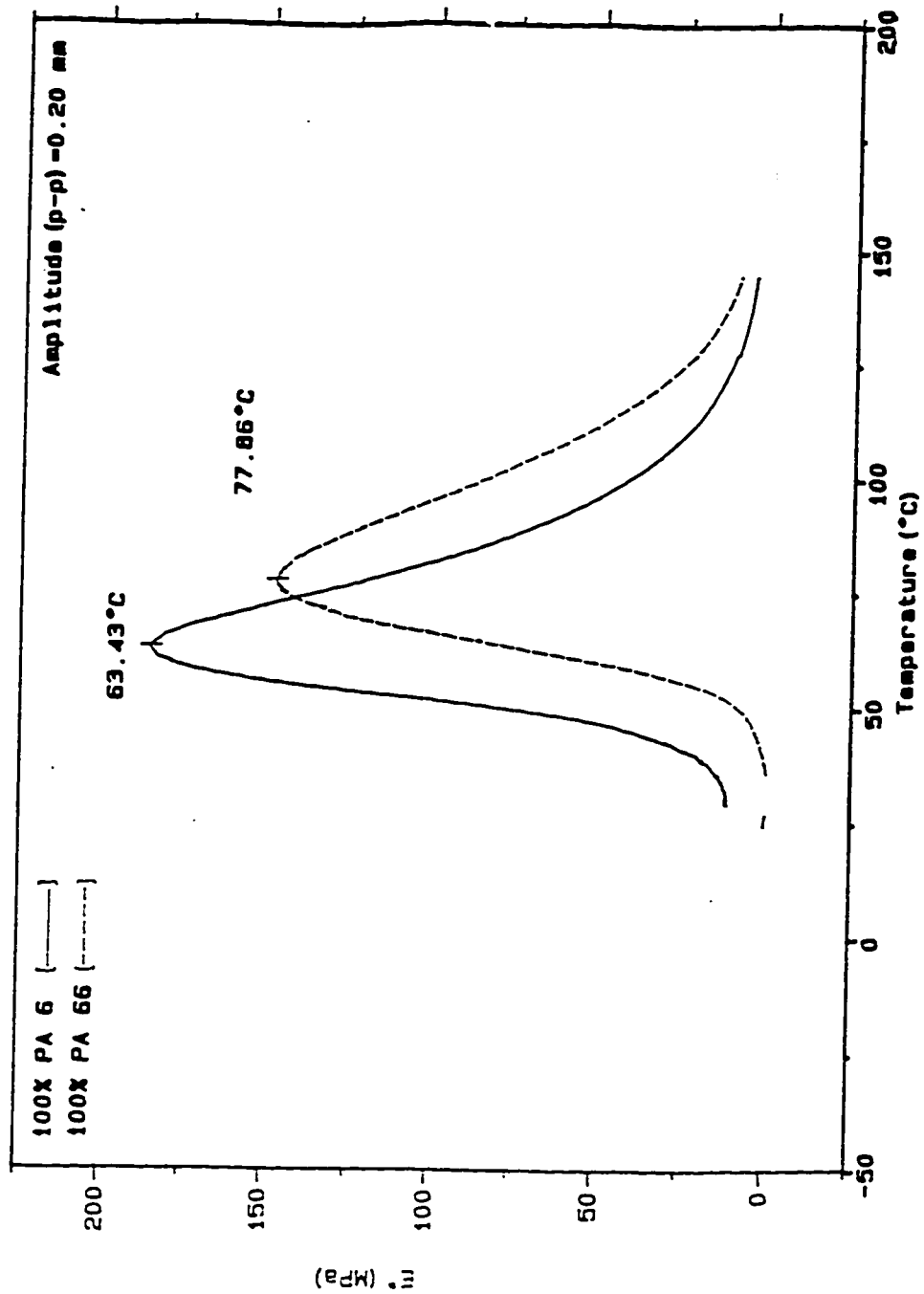
Figure 8. Damping behavior of pure samples.

The damping behavior of the blend samples is illustrated in Figure 9. Several distinct features can be observed from Figure 9. The peak maximum shifts to higher temperatures from the 50% blend, which has a value of 69 C, to the 5% blend with a value of 78.7 C. This trend is shown in Figure 10, which displays the glass transition temperatures as a function of composition. As can be seen, the temperatures go through a slight maximum, with the 5% blend shifted out of the pure component range by about 1 C. For most blend systems, the blend transition values usually fall exclusively between the pure component values, however a shifting to higher values has been observed in certain blends (7).

For completely miscible blends, the Tg of the blend usually has a value that represents the weighted average for the two pure polymers (13). Table 5 shows the calculated weight average, based on the amount of amorphous material in the blends, along with the values obtained by DMA.

Table 5. Calculated and observed Tg's for blends.

% PA 6	Amorphous Fraction Weight Av. Tg (C)	Observed Tg (C)
50	69.4	69.0
35	71.5	71.0
10	75.8	75.6
5	76.8	78.7

As seen in Table 5, the values for the observed Tg and the calculated Tg for the 10%,

35%, and 50% blends are very close. This would seem to indicate a level of miscibility between the components.
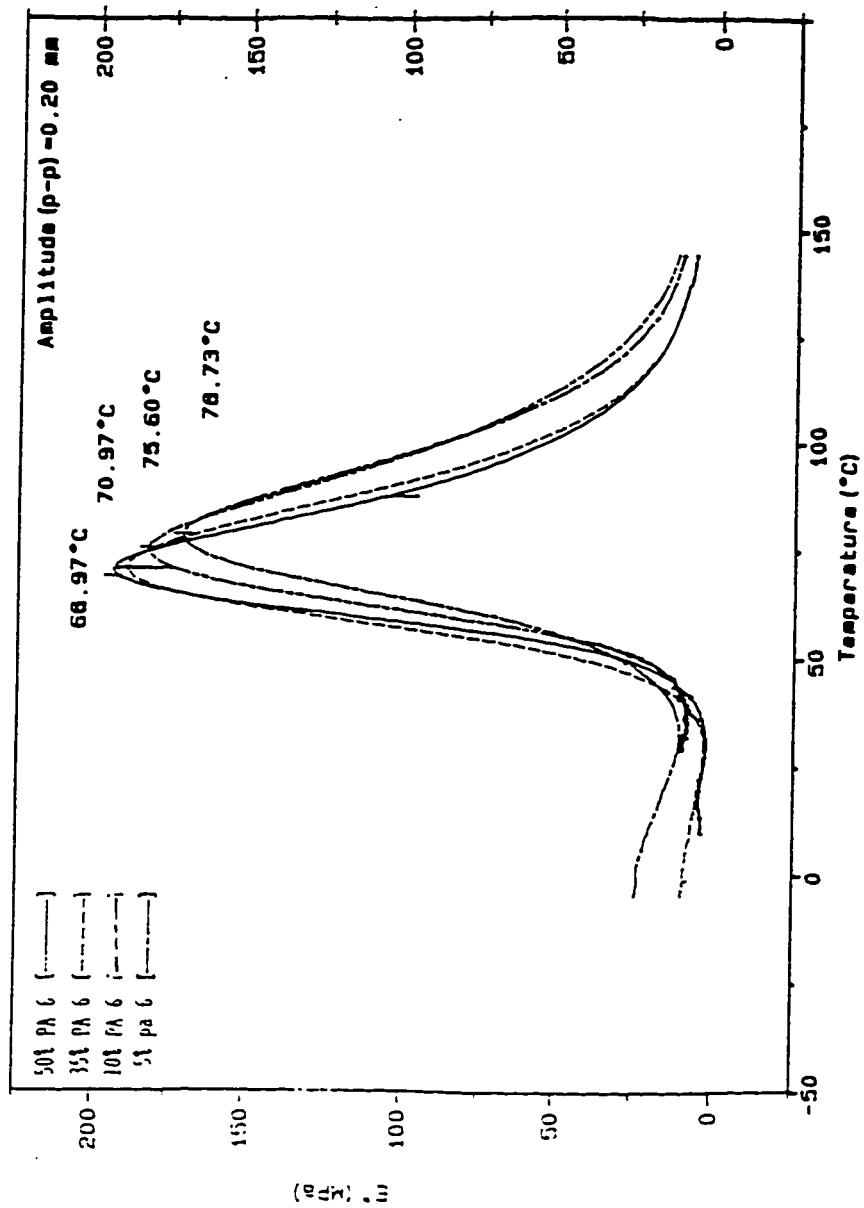

Figure 9. Damping behavior of blend samples.
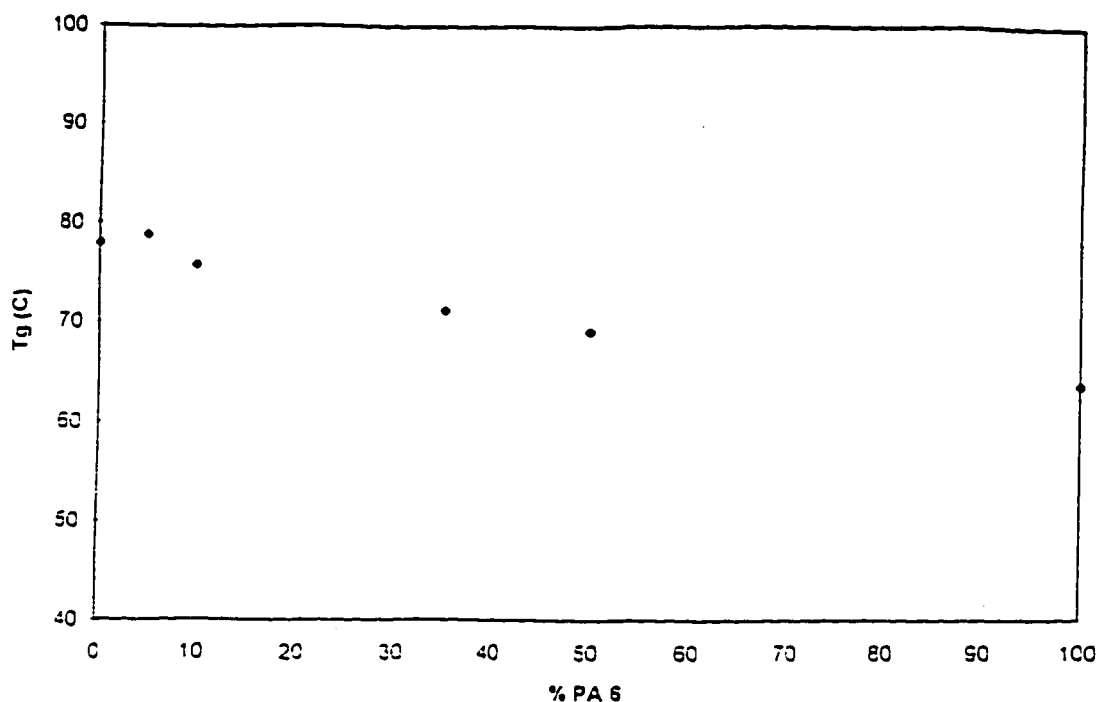
Figure 10. Glass transition temperature versus composition.

Also seen from Table 5 is the higher value for the observed Tg in the 5% blend than for the weight average Tg. This value is also higher than the value for the pure nylon 6,6 polymer, 77.9 C.

The question as to whether the higher value for the 5% Tg is a result of a morphological effect or rather possible water pick up of the pure 6,6 blend, which would shift it to a lower temperature, might be answered by observing the values of the damping curves near 25 C. As will be seen in the following section (Figure 12) the initial values of the damping for "wet" samples is in the 25-30 MPa range, while that for the "dry" samples, Figure 9, are in the 0-10 MPa range. The curve for the 5% sample in Figure

9 shows a value of about 10 MPa near 25 C, while the value for the nylon 6,6 sample in Figure 8 is 0 MPa. This indicates that the 5% blend may have a slightly higher water content than the 6,6 sample. This would likely mean that the transition value for the 5% blend is actually slightly higher than the pure 6,6 sample and not simply caused by a wet nylon 6,6 sample. In fact if the 5% blend were dried giving it a lower initial damping value, as with the 6,6 sample, the transition would likely shift to an even higher temperature, due to the ability of water to cause downward shifts in transition temperatures for nylons (4). This may suggest that a morphological effect may be involved. The size of spherulites in samples of equivalent crystallinities can have different effects on mechanical behavior (4). If the size of the spherulites were decreased in the 5% sample, due to the addition of nylon 6, without a large decrease in the total crystallinity, the effect may be to increase chain stiffness in the amorphous regions. Many smaller spherulites, as opposed to fewer and larger ones, would tend to have a crosslinking effect, the result of which may be to shift the transition to a higher temperature.

Also seen from Figure 9 is the downward shift in the values for the peak maxima over the range from 50% to 5% nylon 6. This behavior is illustrated in Figure 11.
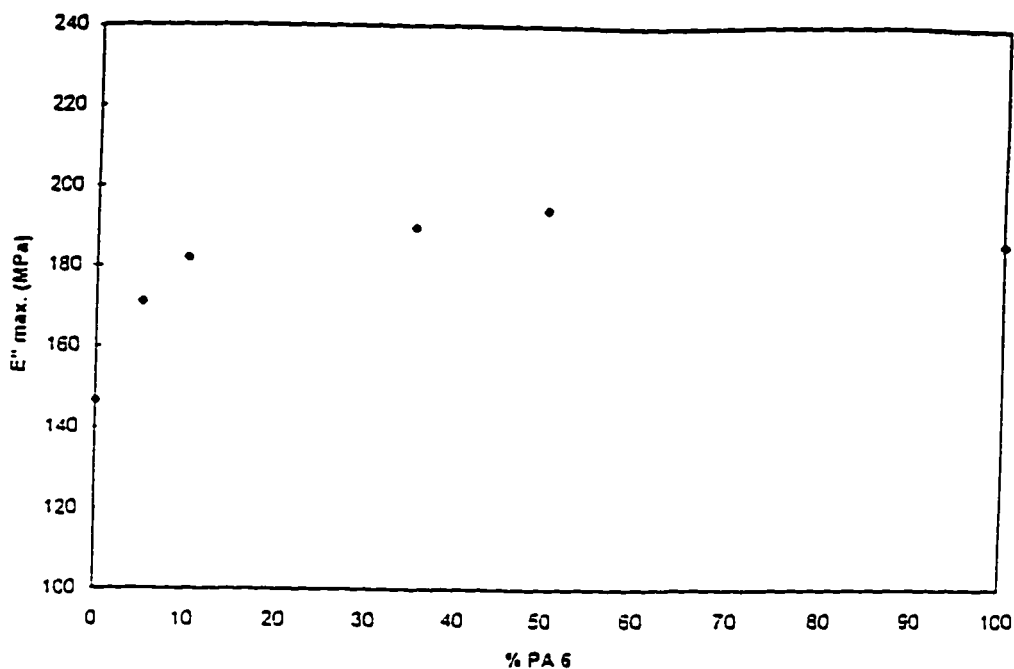
Figure 11. E" maximum versus composition.

As can be seen from Figure 11, the values for E" maxima show a synergistic behavior, going through a maximum at the 50% composition, then decreasing toward the nylon 6,6 value as the blends become enriched in nylon 6,6. The higher values of E" for the 35% and 50% blends may be related to their lower levels of total crystallinity. The presence of more amorphous material in these blends would tend to increase energy dissipation at the glass transition, resulting in the higher value for E". Also notable from Figure 9 are the shapes of the damping curves. For immiscible systems, damping curves will either display two peaks, shoulders on peaks, or peaks which are substantially broader than those of the pure components, depending on how separated the pure

component transitions are (5). The curves in all blends are fairly symmetrical, with no evidence of shoulders, and only a slight increase in broadness from the 50% to 5% blends, that appears to fall between that of the two component samples, Figure 8. Because the pure components are separated by only 15 C, the most one would expect to see for immiscibility would be shoulders or significant broadening of the peaks. These results would seem to indicate, therefore, a level of miscibility between the chains in the amorphous regions.

4.3.2 EFFECT OF WATER

Water can have a profound influence on the transition temperatures of nylons. Water molecules disrupt hydrogen bonding in the amorphous regions, allowing chains greater mobility and subsequently lowering the transition temperatures. A nearly dry sample of nylon 6,6, for example, will have a glass transition of around 80 C, while a sample saturated with water (8% water) will have its glass transition lowered to about -15 C (4).

The samples tested in the previous section were stored in airtight plastic, and thus tested dry as molded. A second set of samples were tested which had approximately two months exposure to air with a corresponding moisture pick up (approximately 1.0 %). Figure 12 shows the effect of water on the damping behavior of the pure nylon 6,6 samples. As can be seen, the temperature of the transition decreases from 77.9 C to 71.8 C, a result which is widely accepted as the result of water plasticization in the amorphous regions (4). Also evident is a decrease in the magnitude and a broadening of the damping

peak. As mentioned in the previous section, the value of the damping near 25 C for dry sample is near zero, while that for the "wet" sample is closer to 25 MPa. Because water disrupts hydrogen bonding in the amorphous sections of the polymer (4), the chains in the wet sample would most likely be more mobile, causing greater ability to dissipate energy and thus a higher damping value at lower temperatures than the dry sample. The dry samples, which have nearly complete hydrogen bond formation in the amorphous regions (5), will have less chain mobility and thus lower damping values at the lower temperatures.
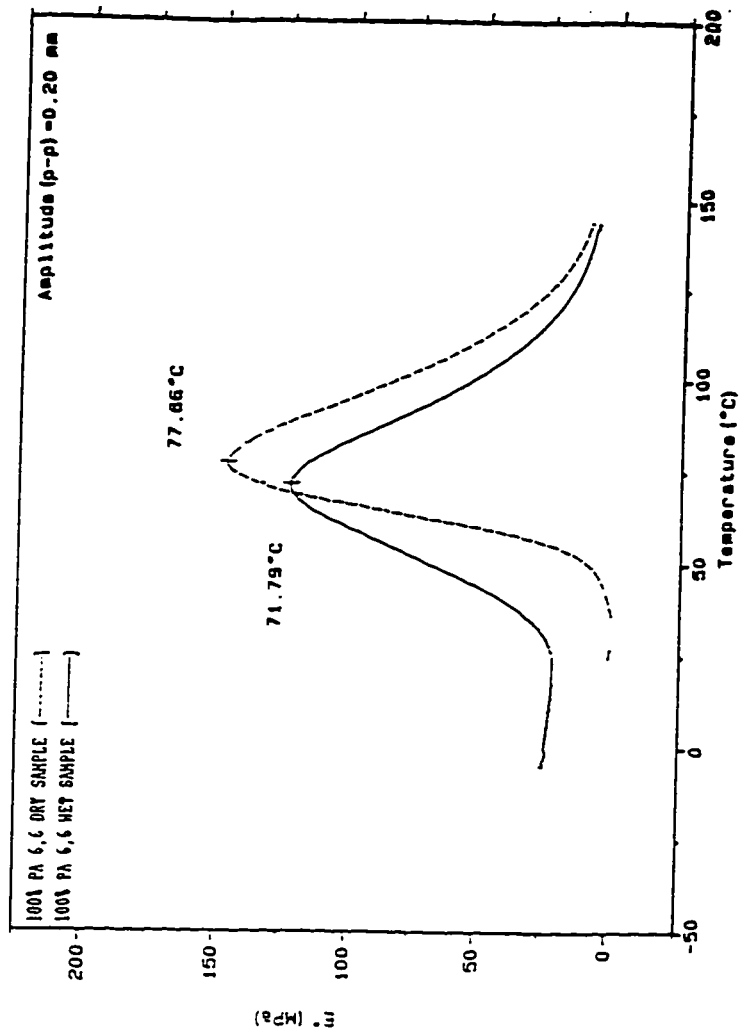
Figure 12. Effect of water on Nylon 6,6 transition.

Figure 13 shows the effects of water pick up for the 50%, 35%, and 5% blend samples. As with nylon 6,6, the wet samples show a decrease in the peak temperatures and maxima as compared to the dry samples.

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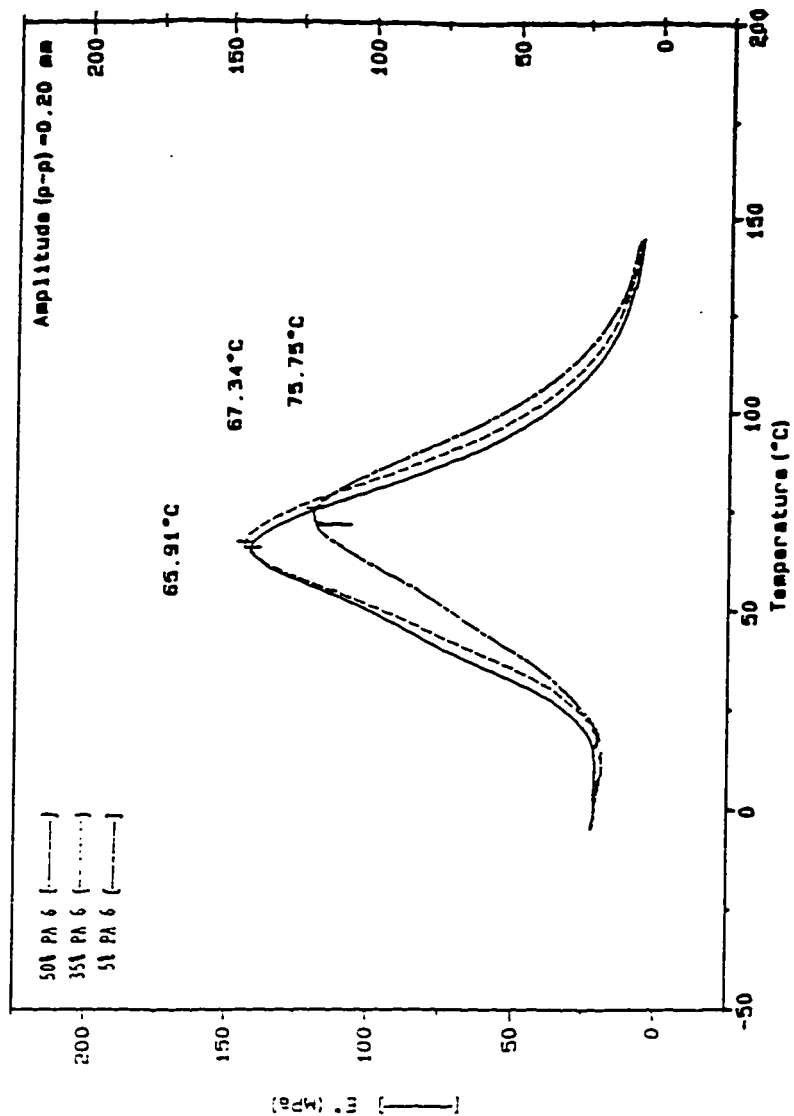
Figure 13. Damping behavior of wet samples.

They also have higher values for damping (25 MPa) near 25 C as opposed to the dry

samples. Substantial broadening along with a slight shoulder on the low temperature side

of the peaks is clearly evident. The broadening may be due to the water molecules

disrupting hydrogen bonds along segments of chains, which could result in some chains starting their relaxations at slightly lower temperatures than those that were still hydrogen bonded.

If miscibility were to be realized for the blends, interactions in the form of hydrogen bonding between the nylon 6 and nylon 6,6 chains would be expected. Water contamination would not only disrupt the bonding between molecules of the same type, but also between nylon 6 and nylon 6,6 molecules if this was indeed occurring. Figure 14 shows the damping curves for the dry and wet 50% blends. The shoulder on the low temperature side of the wet sample may be due to water-affected nylon 6 chains, which in the dry samples would have been bonded to other nylon 6 chains and possibly nylon 6,6 chains, to begin their relaxation at a slightly lower temperature than the chains which were not affected by the water. The effect of water on the nylon 6,6 transition, Figure 12, shows substantial peak broadening, but no shoulders. The shoulder on the blend samples may therefore be due to the nylon 6 component.
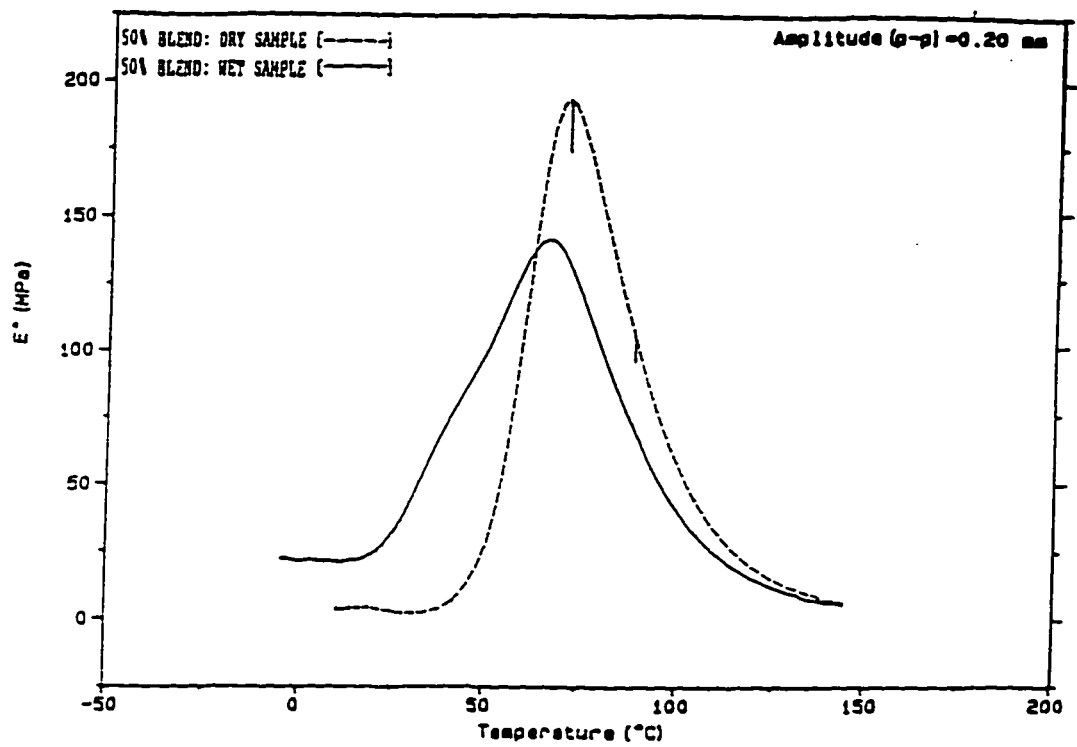
Figure 14. Damping curves for wet and dry 50% blends.

4.4 IMPACT STRENGTH MEASUREMENTS

Izod impact strength measurements were made to determine the effects of blending on the impact strength. Figure 15 shows the breaking energy as a function of blend composition for the various blends.
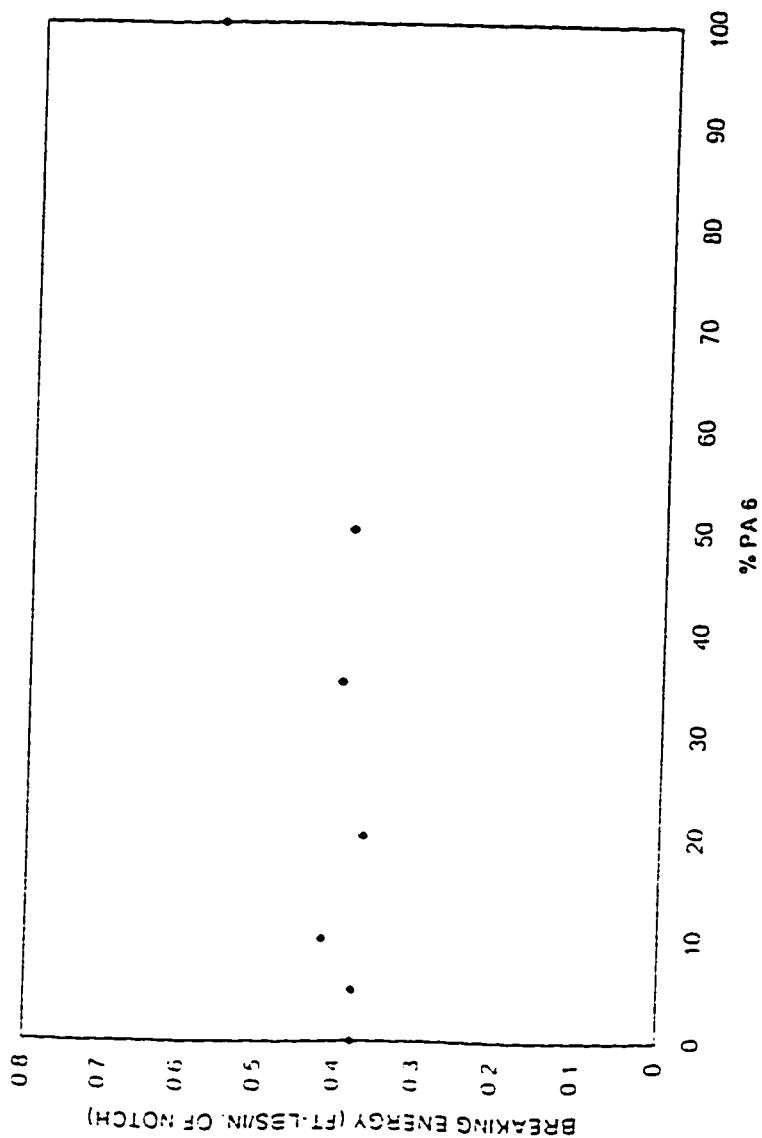

Figure 15. Breaking energy (ft-lbs/inch of notch) versus composition.

The nylon 6 sample shows the highest value for the breaking energy of all the samples, 0.57 ft-lbs/ inch, compared to a value of 0.38 ft-lbs/inch for the nylon 6,6 sample. Values of the breaking energy for each of the blends, however, show very little change from the nylon 6,6 value. As can be seen from Figure 15, the 50% blend has a value almost identical to that of the nylon 6,6 sample. The addition of the tougher nylon 6 component, shows very little effect on the impact strength. Figure 15 would therefore indicate a negative blending effect for the impact strength, giving values lower than those calculated from the weighted averages.

Crystallinity has a profound influence on the impact strength. Higher crystallinities generally give lower impact strengths (5). The total crystallinity of each of the blends decreased from 33% for the 5% blend to about 27% for the 50% blend (Appendix B). Although the total crystallinity of the 50% blend was about 7% less than the value for the pure nylon 6,6 sample (34%), they both had very similar values for the breaking energy. The remaining blends showed a similar behavior.

This behavior may be due to the fact that nylons are very notch sensitive (4), and decreases in total crystallinity of 7% may not be able to produce a significant effect on notched samples. Unnotched samples for each blend produced no break. This may suggest that testing unnotched samples on a higher capacity machine may produce results which better reflect the differences in crystallinity.

CHAPTER 5

CONCLUSIONS

Thermal and mechanical analysis of nylon 6 and nylon 6,6 blends has been carried out in an attempt to determine the behavior of the blends in the crystalline and amorphous regions of the polymer. The resulting effects due to the blending of these two polymers on the impact strength were also determined.

Results of DSC tests indicate the possibility of at least a partial miscibility between the nylon 6 and nylon 6,6 chains. DSC results showed higher values for normalized fusion enthalpies for the blends than for the pure components, indicating a possible interaction between the components which may result in an increase in the crystallization rate. DSC results also show a lowering of the melting temperature of the nylon 6,6 component for the 20%, 35%, and 50% blends. This behavior may be due to a thermodynamic melting point depression, although a morphological effect, in the form of poorer quality crystals may also be contributing to the lowering of the melting point.

The results of the DMA experiments also indicate the possibility of some level of miscibility. Damping curves for blends showed no significant broadening or shoulders which would indicate large scale phase separation. The 5% blend transition was also shifted above the transition temperature of nylon 6,6. This may have been due to changes in spherulite size in this blend, compared to the pure sample, which may have reduced the ability of the nylon 6,6 chains to relax and dissipate energy, thus shifting the

relaxation to a higher temperature. DMA tests on water contaminated samples, however, showed shoulders on the low temperature side and significant peak broadening. The disruption of hydrogen bonding by the presence of the water molecules would likely lead to different chains undergoing relaxations at slightly different temperatures which were able to be observed by DMA.

The results of the impact strength tests showed very little sensitivity to the amount of crystallinity in the blend samples. The blends, which had lower total crystallinities than the pure samples, had impact values that were virtually similar to that of the nylon 6,6 sample. This result may have been due to nylon's high level of notch sensitivity. Testing of unnotched samples may provide more sensitivity to the changes in crystallinity. Performing other mechanical tests that are sensitive to the level of crystallinity, such as tensile tests, may also provide better insight into the effect of the level of crystallinity.

These results may indicate an economic advantage to blending these polymers. Depending on the supplier, nylon 6 ranges from 9% to 40% less in cost than nylon 6,6. Blending of the polymers in compositions of around 25% or less nylon 6 (which results in no nylon 6 crystallization) produces little change in the properties studied. For the 20% blend, for example, the melting point of the blend decreases by only 1.5 C, while the impact strength remained virtually unchanged from the pure 6,6 value. DMA studies show similar small decreases in glass transition values, and also indicate levels of miscibility between the components. Blending of up to 25% nylon 6 could therefore produce significant cost savings in large production runs.

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REFERENCES

1. Deanin and Rudolph, "Practical Benefits of Polymer Blending" <u>Advances in Polymer Blends and Alloys Technology</u>, Vol. 3, pg 1-10, 1992.

2. Stevens, M., <u>Polymer Chemistry, An Introduction</u>, Oxford University Press, pg. 100-104, 1990.

3. Kienzle, S., "Polymer Blends and Alloys: Expanding Opportunities for Plastics", <u>Advances in Polymer Blends and Alloys Technology</u>, Vol. 1, pg. 1-11, 1988.

4. Kohan, M., Editor, <u>Nylon Plastics</u>, John Wiley and Sons, 1973.

5. <u>Encyclopedia of Polymer Science and Engineering</u>, Volume 11, pgs. 315-375, and pgs. 445-475, John Wiley and Sons, 1988.

6. Sperling,L., Taylor, D., Kirkpatric, M., George, H., and Bardman, D., " Glass Rubber Transition Behavior and Compatibility of Polymer Pairs: Poly(ethyl acrylate) and Poly(methyl methacrylate)', <u>Journal of Applied Polymer Science</u>, Vol. 14, pg. 73, 1969.

7. Berstein, R., Paul, D., and Barlow, J., " Polymer Blends Containing Poly(Vinylidene Fluoride). Part 2: Poly(Vinylesters) ", <u>Polymer Engineering and Science</u>, Vol. 18, No. 9, Pgs. 683-686, 1978.

8. Schurer, J., deBoer, A., and Challa, G., " Influence of Tacticity of Poly(Methylmethacrylate) on the Compatibility with Poly(Vinyl chloride), <u>Polymer</u>, Vol. 16, Pgs. 201-204, 1975.

9.   MacKnight, W., Stoelting, J., and Karasz, F., " Physical Properties of the System: Poly(2,6-dimethylphenylene oxide)-Polystyrene", Multicomponent Polymer Systems, Gould, R., Editor, American Chemical Society Publications, 1971.

10. Yee, A. F., " Mechanical Properties of Two Compatible Polymers ", Polymer Engineering and Science, Vol. 17, Pgs. 213-219, 1977.

11. Mekhilef, N., Elbirli, B., and Baouz, T., " Mechanical Behavior of Blends of Polystyrene with Styrene-Isoprene-Styrene (SIS) and Ethylene-Propylene Rubber (EPR) ", Advances in Polymer Blends and Alloys Technology, Kohudic, M., and Finlayson, K., Editors, Vol. 2, Technomic Publishing, 1989.

12. Chin, W., and Hwang, J., " Modification of (ABS) Properties by Additions of Polycarbonate (PC) and Nylon 6 ", Advances in Polymer Blends and Alloys Technology, Kohudic, M., Editor, Vol. 1, Technomic Publishing, 1988.

13. Manson, J., and Sperling, L., Polymer Blends and Composites, Plenum Press, Pgs. 51-75, 1976.

14. Rybnikar, F., and Geil, P., " Interactions at the PA-6/PA-66 Interface ", Journal of Applied Polymer Science, Vol. 46, Pgs. 797-803, 1992.

15. Ellis, T., " Mixing Relationships in Aliphatic Polyamide Blends ", Polymer, Vol. 37, Pgs. 1469-1476, 1992.

16. Verma, A., Deopura, B., and Sengupta, A., " A Study on Blends of Nylon-6 and Nylon-66, Journal of Applied Polymer Science, Vol. 31, Pg. 747-762, 1986.

17. Whelan, T., and Goff, J., Injection Molding of Engineering Thermoplastics, VanNostrand Reinhold, pg. 60-86, 1990.

18. Sweet, G., and Bell, J., " Multiple Endotherm Melting Behavior in Relation to Polymer Morphology", Polymer, 1972.

19. Nishi, T., and Wang., T., "Melting Point Depression and Kinetic Effects of Cooling on Crystallization in Poly(vinylidene fluoride) Poly(methyl methacrylate) Mixtures", Macromolecules, Vol. 8, pages 909-915, 1975.

APPENDIX A: SAMPLE CALCULATIONS

A.1 Calculation of Normalized Fusion Enthalpies

Fusion enthalpies were determined from the area under the endotherm peak of the

DSC scans. The area was integrated by the DSC software between two temperatures

which represented the endothermic deviations from the baseline. These integration limits

were user supplied, and an example of the baseline construction is illustrated in Figure
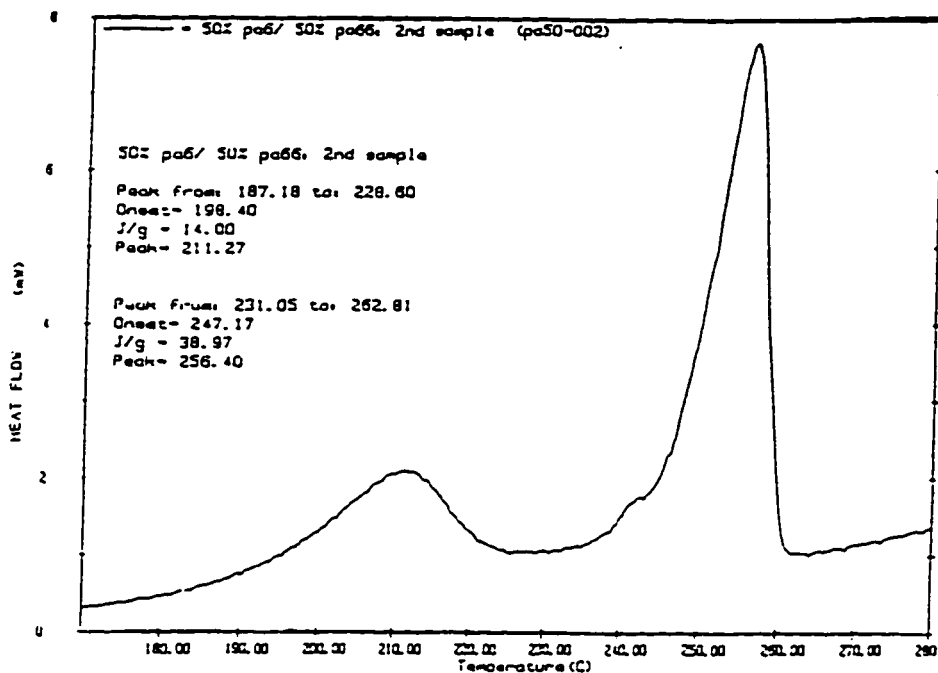
16.

Figure 16. Baseline determination for peak integration.

For this example, the 50% blend, the limits for the first peak were taken as 187.2 C to

228.6 C, and for the second peak 231.1 C to 262.8 C. These values were also used for

the 35% blend, while the limits of 235.0 C to 262.0 C were used for the remaining

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samples. Computer integration of the resulting peaks gave the following values for the fusion enthalpies:

$$Hf1 = 14.00 \text{ J/g}$$

$$Hf2 = 38.97 \text{ J/g.}$$

These values were next normalized to weight percent of each component in the blend to give the final values for the fusion enthalpy.

$$nHf1 = Hf1/wt.\% = 14.0/0.5 = 28.0 \text{ J/g}$$

$$nHf2 = Hf1/wt.\% = 38.97/0.5 = 77.9 \text{ J/g.}$$

Note: All values are ± 0.1 J/g.

A.2 Calculation of Percent Crystallinity

The percent crystallinity of each component was determined by dividing the calculated value of the fusion enthalpy by the theoretical fusion enthalpy of a 100% crystalline sample, which was taken from the literature (5). For the 50% blend, the percent crystallinity was determined as follows;

$$\% \text{ cryst. PA 6} = (nHf1/ 190 \text{ J/g}) * 100 = (28.0/190) * 100 = 14.7\%$$

$$\% \text{ cryst. PA6,6} = (nHf2/ 196 \text{ J/g}) * 100 = (77.9/196) * 100 = 37.7\%$$

A.3 Calculation of the Theoretical Melting Point Depression

The following equation was used to calculate the expected melting point depression for

the 10% blend.

$$\frac{1}{Tm} - \frac{1}{Tm^o} = \frac{R\ V2u}{H2u\ V1u}\ X12\ (1-V2)^2$$

where, 1 refers to PA 6 and 2 refers to PA 6,6

Tm = melting point of crystalline polymer in blend

Tm^o = melting point of pure polymer

Vu = molar volume of repeat unit

V = volume fraction

R = Gas constant

H = fusion enthalpy

X12 = Flory interaction parameter

Taking the following values,

V1u = 113.16 g/mol / 0.96 g/cm^3 = 117.88 cm^3/mol

V2u = 226.32 g/mol / 0.99 g/cm^3 = 228.84 cm^3/mol

H2 = 15367.13 J/g

Tm^o = 261.1 C

R = 8.314 J/mol K

X12 = -0.3.

Substituting these values into the previous equation would yield a value of 260.84 for Tm.

A.4 Calculation of the Breaking Energy

The breaking energy was calculated by taking the value from the indicator dial on the impact tester in Ft-lbs and multiplying by 4 to convert the value from ft-lbs/ 0.25 in of notch (samples were 1/4 ") to a value of ft-lbs / in of notch.

APPENDIX B: EXPERIMENTAL DATA

B.1 DSC Data

Table 6. Summary of DSC Data.

% PA 6	Tm1(C±0.1)	Tm2(C±0.1)	Hf1 (J/g ± 0.1)	Hf2 (J/g ± 0.1)
0	---	261.1	---	67.9
5	---	261.2	---	68.3
10	---	261.0	---	66.5
20	---	259.6	---	70.7
35	209.9	258.7	18.0	73.8
50	211.3	256.4	28.0	77.9
100	219.2	---	57.7	---

Where 1 refers to PA 6, and 2 refers to PA 6,6

Table 7. Total crystallinity versus composition.

% PA 6	% TOTAL CRYSTALLINITY
0	34.6
5	33.2
10	30.5
20	28.9
35	27.7
50	27.3
100	30.4

B.2 DMA Data

Table 8. Summary of DMA data, dry samples.

%PA 6	Tg (C±0.1)	E"max. (MPa)
0	77.9	147.6
5	78.7	171.0
10	75.6	181.8
35	71.0	189.5
50	69.0	194.3
100	63.4	185.1

Table 9. Summary of DMA data, wet samples.

%PA 6	Tg (C±0.1)
0	71.8
5	75.8
35	67.3
50	65.9

B.3 Impact strength data

Table 10. Impact strength data

Breaking Energy (ft-lb/inch of notch±0.01)						
pa 6	5%	10%	20%	35%	50%	pa 66
0.12	0.10	0.09	0.10	0.10	0.09	0.10
0.13	0.11	0.11	0.11	0.11	0.09	0.10
0.13	0.10	0.10	0.09	0.08	0.10	0.09
0.17	0.09	0.11	0.09	0.10	0.11	0.10
0.15	0.09	0.12	0.09	0.10	0.11	0.09
0.14	0.11	0.11	0.09	0.10	0.10	0.10
0.15	0.09	0.10	0.09	0.10	0.09	0.09
0.11	0.09	0.09	0.09	0.10	0.09	0.09
---	0.09	0.12	0.09	0.11	0.10	0.10
Av. 0.14	0.10	0.11	0.09	0.10	0.10	0.10

APPENDIX C: CALIBRATION DATA

C.1 DSC Calibration

A two point calibration of the DSC was preformed with indium and zinc standards. The procedure consisted of running both samples 30 C past their melting points and recording the melting points and heats of fusion. These values were then re-entered into the DSC which used them to preform an internal calibration. The results are summarized in Table 11.

Table 11. DSC calibration Data.

Sample	Tm(C)	Hf(J/g)
Indium (first run)	158.3	27.96
Zinc	422.3	113.36
Indium (after internal calib.)	155.1	28.56

C.2 DMA Calibration Data

The DMA was calibrated according to the manufacturers instructions. The calibration consisted of calculating constants to correct for instrument contributions to modulus calculations, and a temperature calibration. The temperature calibration consisted of running a polycarbonate sample at 1 Hz. fixed frequency and entering the value for the peak maximum of the E" curve (153.0 C) into the software. The computer then corrected

the temperature.

The instrument calibrations consisted of six calibration procedures, the results of which are summarized below. All values fell within the manufacturers established parameters.

```
         .INERTIAL MOMENT

Added Weight    Wc    50.00 g
Arm Position (no weight)    PO:    0.140 mm
Arm Position (with weight)  Pwc    0.265 mm
Frequency  f:    18.10 Hz

Inertial Moment  J:    2.49 g-m^2

         SPRING CONSTANT

Freq. free arm  f0:    1.90 Hz

Parallel Storage Stiffness  K':    0.355 N-m

         DRIVE SIGNAL CONSTANT

Osc Amplitude   an:    0.20 mm
Frequency  fn:         17.97 Hz
Drive Signal  Vn:      24.43 mV
Drive Transfer  VO/AO: 14304.78 mV/mm

Drive Signal Constant  C':    0.0225 mm/(mV-sec^2)

Parallel Loss Stiffness  Kn':    0.271 N-m   at    17.97 Hz

         SERIES COMPLIANCE

Osc Amplitude   ac:    0.05 mm
Frequency  fc:         88.72 Hz
Drive Signal  Vc:      950.24 mV
Size:    28.15 X  12.78 X  2.90 mm

fc:    166.12 Hz
Maximum Frequency (f infinity):    104.93 Hz

Series Storage Compliance  Jc':    0.901 um/N

Series Loss Compliance  Jcm':    0.0476 um/N  at    88.72 Hz

         PHASE ZERO CALIBRATION

Standard deviation of fit:    0.0004 rad
```

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C.3 Impact Strength Calibration

The impact tester was calibrated by adjusting the dial on the breaking energy scale to give a value of 0 ± 0.01 ft-lbs for a hammer swing with no sample in the vise.