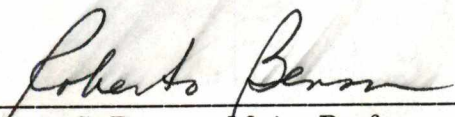
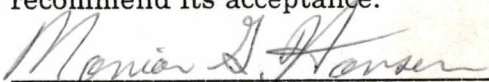


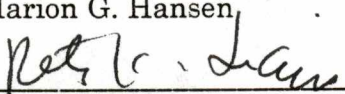
To the Graduate Council

I am submitting herewith a thesis written by Daryl W. Grummitt entitled "Mechanical and Morphological Characterization of Polyamide Bone Analogues." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.


Roberto S. Benson, Major Professor

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recommend its acceptance:


Marion G. Hansen


Peter K. Liaw

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Associate Vice Chancellor and
Dean of the Graduate School

**MECHANICAL AND MORPHOLOGICAL CHARACTERIZATION
OF POLYAMIDE BONE ANALOGUES**

A Thesis

Presented for the

Master of Science Degree

The University of Tennessee, Knoxville

Daryl W. Grummitt

May, 1996

DEDICATION

This Thesis is dedicated to
Mr. David Grummitt and Mrs. Janet Grummitt
for their continued love and support.

ACKNOWLEDGMENTS

So many have contributed to making my experiences here at the University of Tennessee both fun and educational. I have to thank those in the Materials Science and Engineering department, faculty and students, graduate and undergraduate that have helped to enrich my life. Specifically I want to recognize my advisor Dr. Roberto Benson and committee members Dr. Marion Hansen and Dr. Peter Liaw for their support of this project. Additionally, I couldn't have done it without the contributions from my fellow group members Darnell Worley II and Steve Lee as well as all my friends that helped me through the past two years. The thoughts presented here in this thesis have all been influenced by these wonderful people.

Financially I would like to thank the Plastics Institute of America, Inc. (PIA) for their personal grant towards this work. The support was well appreciated and my thanks goes specifically towards William Sacks, Executive Director for the Institute.

Last, and most importantly I thank my parents and family. They have supported me all of these years in every endeavor, not the least bit wavering in believing that I could accomplish my goals.

ABSTRACT

This research was an investigation for finding a suitable materials to model the mechanical properties of human bone. Polymer/ceramic particulate filled composites were used to achieve these objectives. The resin used as a matrix was nylon 6 and the particulate fillers were calcium and phosphate salts, CaCl_2 and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$). An analysis of the thermal and morphological properties was performed and these findings were related to the results of the mechanical data.

Blend compositions ranged from a weight percent of 0.5 to 10% salt in the polymer matrix. Most analysis was performed on blends created by a solution mixing method, which facilitated interaction of the two phases. The results from the mechanical data were fitted to theoretical predictions for particulate composites. The theories used included the Sato-Furukawa prediction for reduced modulus, (E/E_1) , the Kerner model for ultimate tensile stress, and the Nielsen prediction for breaking strain.

All blend samples exhibited a reduction in modulus from that of the pure material. The hydroxyapatite blends agreed well with the Sato-Furukawa prediction for this reduced modulus as a result of cavitation. CaCl_2 blends exhibited an increase in tensile strength, which was contrary to that of the hydroxyapatite samples. Thermal properties showed that the 5.0% and 6.0% CaCl_2 blends exhibited little, or no crystallization behavior. Comparisons of the 10.0% hydroxyapatite to that of reported values for trabecular bone agree favorably in the areas of tensile strength, strain to break, and to a lesser degree, elastic modulus. From these findings and previous research the composition of a full bone analogue is proposed and discussed .

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INTRODUCTION

Death and injuries caused by automobile as well as motorcycle accidents currently number 16.1 per 100,000 per year. This is roughly equivalent to all other accidents combined.[1](NCHS, 1995) Hence, automobile manufacturers are continuously looking for new ways to protect the driver and occupants from serious injury and/or death. Those that are not killed sustain severe injuries, such as spinal injury, at the rate of approximately 10,000 per year.

To help reduce these fatalities Hybrid III test dummies have traditionally been used to determine the accelerations and motions of human passengers in automobile impact studies. These anthropomorphic systems of pressure transducers have led to many design changes and developments for the industry such as additional padding, seat belt modifications, and most notably, air bags. Studies have been conducted to determine the numbers of various injuries sustained. The injuries themselves are categorized by way of the Abbreviated Injury Scale (AIS) and represent the degree by which they debilitate the subject.[2](Ward) Table 1 shows that in frontal impact studies the legs are the second highest severe injury recorded. Although head, face, and chest injuries

Table 1. Automobile occupant injuries with AIS 2 or greater by body region.

Body region	Frequency	Percent of 658 samples
Head and Face	314	48
Legs	214	33
Chest	202	31
Arms	167	25
Abdomen	42	6
Neck	22	3

represent a large portion, this study was performed before 1991, when most cars were not equipped with air bags.

The lack of breakable elements on Hybrid III test dummies is a particular limitation with impact studies. A solution to this problem is the use of cadavers and animal bones for these studies. However, this carries with it many controversial opinions, most notably that animals have a dissimilar geometry to that of humans and should not be used for such studies. As well, human cadaver testing is scrutinized due to the fact that "fresh" human bones break differently than those of preserved samples. Differences are also appreciable between people of varying sizes and shapes and data related to one select group has not yet been tabulated.

A solution to these problems is possible by development of a bone analogue material that can be used in place of cadavers and traditional non-frangible dummies. Due to the varying nature of a bone's structure (hydroxyapatite and collagen fiber matrix) the need for a designer set of materials is evident. For these reasons the strength and engineering ability of polymer blends, or composites make them ideal for producing a substitute for human bone. The ease of processing into molded shapes, e.g. tibia, femur, etc. adds to their functionality as analogues.

Previous studies have shown that polyamide/glass-fiber reinforced materials have similar properties to that of bone. Because of this, the matrix material for this study was chosen as nylon 6. The inherent hydrogen bonding that takes place when nylon 6 crystallizes makes this a suitable matrix material. The fillers, or particulate reinforcement, will be either CaCl_2 or hydroxyapatite (HA). These fillers were chosen based upon their availability as well as their known importance in molecular chain interactions (CaCl_2) and significance in real bone (HA).

The objective is to relate the findings of the mechanical properties to the values of natural bone. To understand possible changes in the various blends due to the fillers , the morphology of the matrix will be observed and related to the properties gained, or lost with their addition. Thermal properties will also be analyzed to help in the development of future processing parameters for molding full size bone specimens.

CHAPTER I

LITERATURE REVIEW

Bone - Natural and Synthetic Approaches

Anatomy of Natural Bone

Wet bone contains 69% inorganic matter, 22% organic matter, and 9% water. The inorganic minerals contained in bone are mainly calcium, phosphate, carbonate, and citrate. The organic matter, which is made up of hundreds of different proteins is found mainly as a fibrous matrix. The matrix is made up of semi-flexible collagen fibrils, which are approximately 300 nm in length, primarily aligned parallel to the major axis.[3](Park) The collagen fibers make up the majority of the structure of bone, accounting for approximately 90-95% of the organic matter. Within this matrix exists the hydroxyapatite (HA) crystals ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), which are approximately 20-40 nm in length and align their primary crystallographic axis parallel to the collagen fibrils. A figure of the general makeup of a human long bone is shown in Figure 1.

The macrostructural anatomy of bone is highly varied throughout the length of the specimen. The center region, or diaphysis, is composed mainly of compact bone covered by a thin shell, or periosteum. The dense construction of compact bone is made up primarily of osteons, or closely packed, concentric lamellar patterns of collagen fibrils. Between the osteons exist interstitial regions of lamellae to fill the gaps. The concentric lamellae, or osteons contain blood vessels interconnected

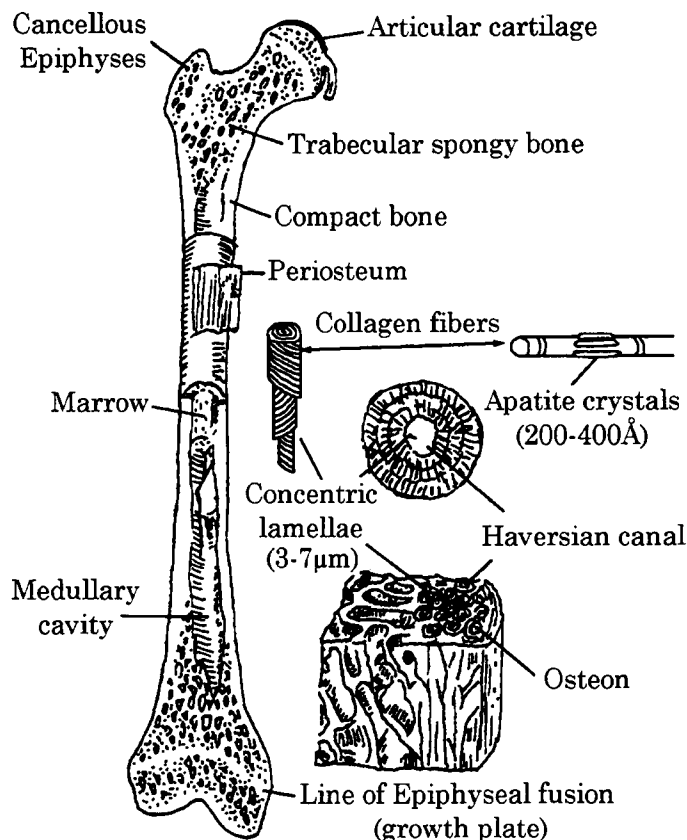


Figure 1. Structure of a human long bone. (adapted from Ref. 3)

by a system called Volkmann's canals. The vessels supply the nutritional needs of the organic material in the bone.

Cancellous and trabecular bone vary from compact bone mostly in density. The makeup of these areas of bone has been compared to that of engineering cellular solids.[4](Gibson). The density can range from approximately 1.05 g/cm^3 to 1.30 g/cm^3 for cancellous and trabecular bone compared to 1.80 g/cm^3 for that of compact bone.[5][6](Rohl)(Carter) However, if the loading conditions in a particular person require more strength in these areas, the uptake of calcium and formation of hydroxyapatite will increase to accommodate the need for structural integrity.

Composite Nature and Properties of Bone

The construction of bone forms a naturally occurring composite material. The effects of the hard, ceramic hydroxyapatite on the collagen form an excellent property balance. This natural hydroxyapatite forms synergistic relationships with the surrounding matrix. The nucleation of hydroxyapatite onto the collagen fiber matrix is facilitated by a matching of the crystal structure to allow a strong interface. This makes bone a natural composite with high modulus particles interspersed in a fiber matrix.

Collagen fiber typically has a modulus of approximately 1.0 GPA.[3](Park) The addition of HA, with a modulus of 144 GPa, to this fibrous network substantially increases the properties.[7](Grenoble) Values of the elastic modulus for human bone samples can range from 1 to more than 250 GPa depending upon the location in the body.[8](Szivek) In the case of compact bone the typical values of Young's modulus are greater than 150 GPa. This variation arises from changes in the amount of hydroxyapatite contained within the bone, thus contributing more, or less, to the mechanical properties. Density, therefore, is an indication of the resulting mechanical properties.

The tensile strength of human bone is representative of a good composite because its strength is higher than either hydroxyapatite or collagen alone. This is due to the collagen matrix preventing premature cracking of the material, while the hydroxyapatite prevents premature yielding. A representative stress-strain curve of a human long bone is shown in Figure 2.[9](Evans) The tensile strength of whole bone typically mirrors the strength of the strongest area of bone, the dense compact bone. This region of bone has tensile strengths ranging in value from

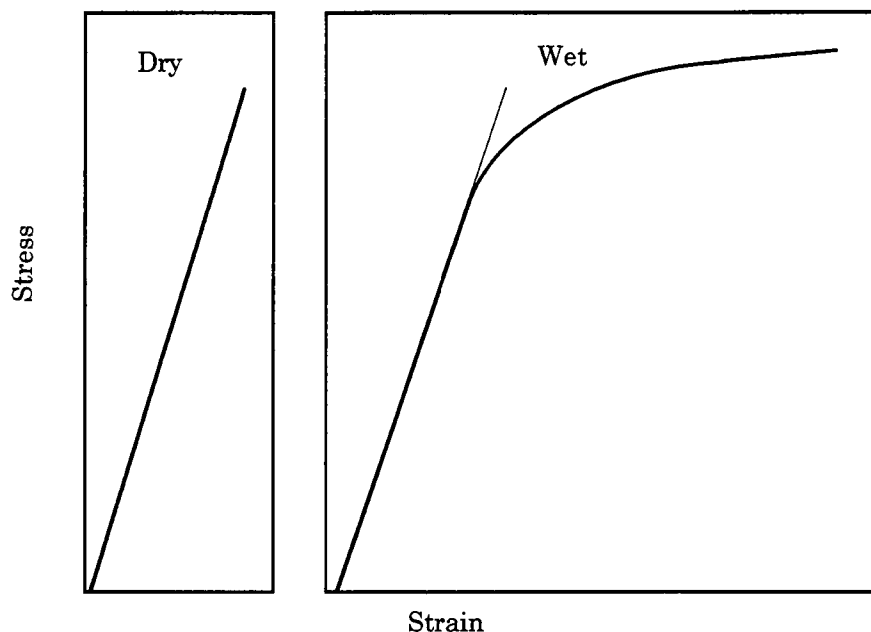


Figure 2. Schematic of stress-strain curves for wet and dry femoral bone.[3](Park)

approximately 70 to 150 MPa depending on the subject.[10](Yamada) In the case of trabecular and cancellous bone (located at the head of the femur and tibia) these tensile values are considerably less, having values of approximately 2-15 MPa.

As illustrated in Figure 2 the strain to break values vary with moisture content. The effect of water is most influential in determining the energy absorption of the material. Although the modulus and ultimate stress do not change significantly, the strain to break changes by a factor of 2 or 3, greatly affecting impact performance. For most bone materials the values of strain typically fall between 1 and 3%.

Bone Analogues

From a materials science viewpoint the composition and excellent strength to weight ratio characteristics of natural bone make the use of polymer composites or filled polymers natural choices for a bone analogue. The processability of fill polymers will allow relatively easy fabrication of realistic shapes that can be used to test not only the tibia and femur, but also more complicated bone structures like the pelvis. In addition to being lightweight, another advantage of polymeric based composites is the ease with which mechanical properties can be tailored to simulate variation in age, shape, size, density, and the possibility of disease.

A number of different possibilities for polymer-polymer composites and polymer-ceramics have been explored. They have helped to provide insight on the project at hand and reveal strengths and weaknesses for various systems. Most, however, additionally focus on the biocompatibility aspects of the material for implant purposes, which limits the number of polymers to use as a matrix.

One recent development geared towards breakable appendages was explored by Newman and Zellner.[11](Newman) They have applied frangible limbs composed of fiber and resin composite to a MATD (Motorcycle Anthropometric Test Device) crash dummy. The frangible tibia and femur were constructed of helical and axial glass fibers bound in a resin matrix. Tests for static bending were performed and the results show similar failure strengths to that of human tibias as reported by Yamada. [9](Yamada)

Szivek et. al. have devised a bone substitute, which could also be used as a mechanical alternative to human bone.[8](Szivek) The bone analogue was a foam based on a polyurethane resin and isocyanate (Daro® foam). Their objective was to create a reproducible material with consistent mechanical properties. The results of

the tests are positive, however they were not extensive. They included only compressive strengths and did not fully explore the methods by which a controlled variation would be introduced.

Polymer-ceramics, however, are the more promising between the composites. Bonfield studied a series of high molecular weight polyethylene(PE)-hydroxyapatite (HA) blends as potential bone substitutes and noted that the Young's modulus could be increased from approximately 1.0 GPa for pure polyethylene to a maximum of approximately 9.0 GPa with a 50% volume fraction of hydroxyapatite.[12](Bonfield) The strain to break varied from greater than 90% for the polyethylene to approximately 3% for the PE with 50% HA. Very little change was observed in the ultimate tensile strength. Tencer et al. have also used polymer and ceramics, but pursued a different approach for the development of a bone substitute.[13](Tencer) In this case, a thin polymeric coating of poly(lactic acid) (PLA) is used in conjunction with a porous substrate of hydroxyapatite. In spite of the initial significant improvement in properties of the material, the coating degrades.

Recently Stupp and Ciegler have synthesized a new family of organoapatites based on poly(amino acids) and apatite crystals.[14](Stupp) They have created a mineral network, which allows the healing process of natural bone to take place. In the mean time, they act as a stable implant to support the body.

Most of the aforementioned studies show no ability to produce bone analogues that can mimic the observed variation in real bone properties such as density, impact strength, age, and moisture. The polyamide-inorganic salt blends selected for use in the proposed study will permit the systematic production of bone analogues which mimic age, density, and wet bones (because nylon is hydroscopic).

The selection of a polyamide-inorganic salt system for the development of a bone analogue is based upon previous work with this system. The mechanical properties of a typical 30% short glass-fiber reinforced nylon 6 are found to compare readily to bone with values of 178 MPa and 2.5% for tensile strength and elongation to break.[15](Modern Plastics) Based upon these values a series of glass fiber reinforced polyamide 6/calcium chloride blends were designed in our labs to have mechanical properties close to those measured for the human tibia. The study was conducted in unison with tests on actual bone to compare the bending impact of the specimens.[16](Snider) The average impact strength found for the tibia and polyamide composites were 18,420 J/m³ and 22,600 J/m³, respectively. Although the tibial testing was bending impact only, the study was also centered around the variation in the thermal and mechanical properties as a function of salt concentration. The specific effects of salt concentration in polyamide resins are discussed more extensively in the next section.

Analogue Constituents

Polycaprolactam

Polycaprolactam, better known as nylon 6, was synthesized first at the laboratories of E.I. duPont de Nemours and Co. The basis for its discovery was work performed by Wallace Carothers on the condensation reactions of polymerization.[17](Mark) This process involves the combination of molecular units with the by-product being a small molecule, such as water. The collective name for the polymers produced by this method from hexamethylenediamine and adipic acid was termed "nylon" by the DuPont company. Because they contain the

carbonamide group, -CONH- they are typically referred to as the polyamide family of thermoplastics.

The first uses for nylon appeared as fibers for toothbrushes. At the time, the new nylons had a thermoplastically unique ability to crystallize upon drawing into fibers. The birth of monofilament line was sprung from this technology and continues today. The applications of the synthetic fibers have grown, but the basic formulations for its production remain relatively untouched. As a bulk material, nylons as well as nylon 6 see many applications requiring reasonable heat resistance, impact toughness, tensile strength, and rigidity.

Synthesis

As its name implies, polycaprolactam is made up of many repeating units of caprolactam. There are typically three ways in which nylon 6 is polymerized. Batch polymerization, or melt phase is the most widely used technique followed by solid-phase, and finally zone-polymerized polycaprolactam.[18,19](Zimmerman) (Saunders) Each of these techniques yields a different type of nylon 6 and are distinguished only by analytical techniques.

The caprolactam is typically referred to as the intermediate for the production of nylon 6 and is produced using a technique called the Beckmann Rearrangement shown in Figure 3.[20](Sherwood)

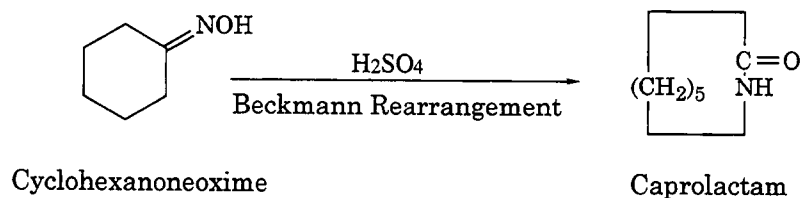


Figure 3. Process of caprolactam synthesis from cyclohexanoneoxime.

The transformation of cyclohexanoneoxime to caprolactam by this method is one step in a series of raw material transformations that must take place to arrive at the appropriate nylon monomers. A more complete representation of the synthesis steps from the raw materials toluene, benzene, and cyclohexane is shown in Figure 4.[21](Hardy) As an aside, one of the resultant intermediaries is also adipic acid, the precursor to nylon 6,6.

Polymerization of the monomer units is performed under pressure at approximately 2500 psi and 200°C.[22](Ogata) Additionally, the reaction will only take place in the presence of water, which is typically added at a concentration of

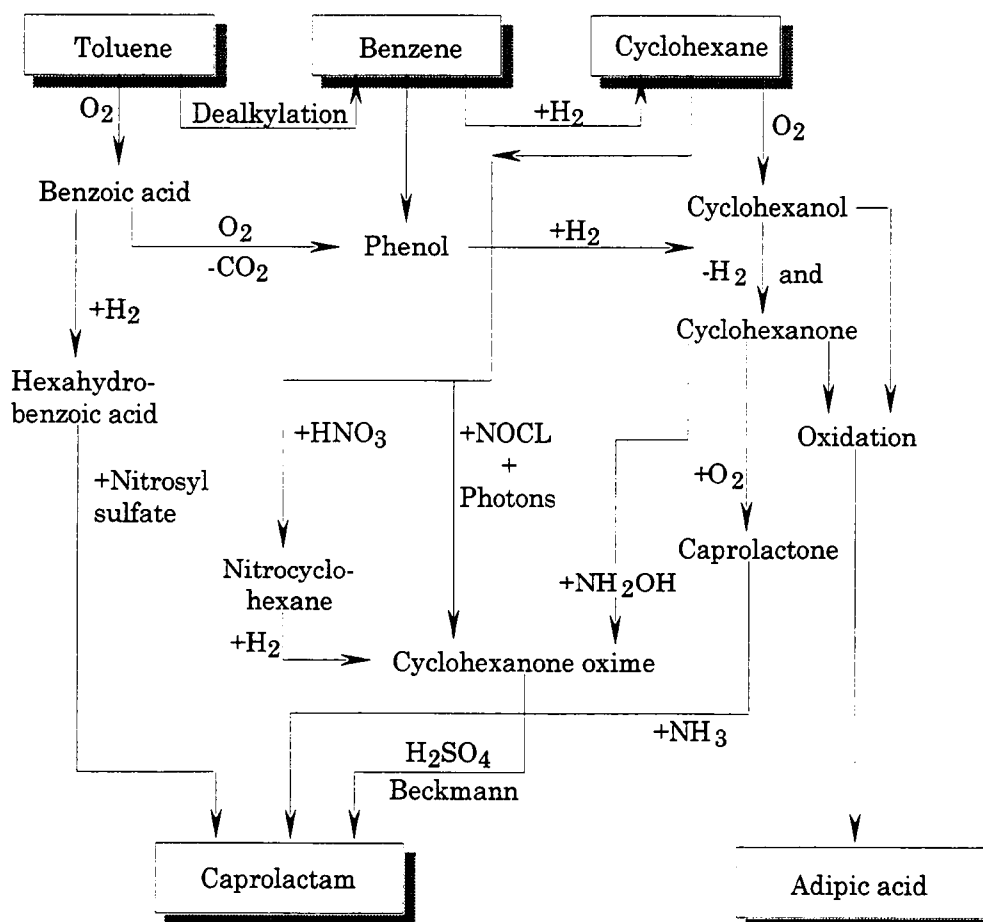
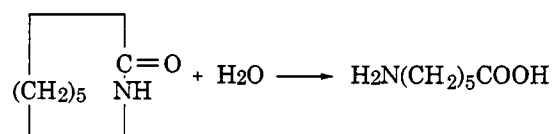
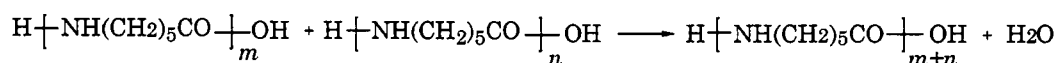


Figure 4. Synthesis of intermediates for nylon 6 (adapted from Ref. 7).

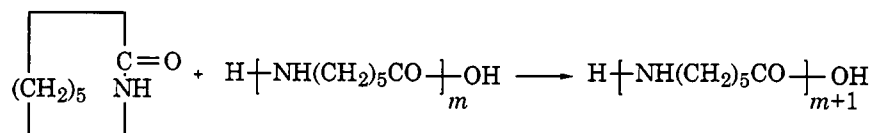
10%.[23](Hermans) The addition of water is essential for nylon 6, which is not the case for nylon 6,6, when pH plays a more important role. Typical pH for a 20% solution of aminocaproic acid and monomer is approximately 5.7.[24](Papero) When polymerizing, the reactions proceed via three mechanisms, which are shown in Figure 5.[23,25-27](Hermans)(Kruissink)(Heikens) Of the three mechanisms, the addition reaction has been found to proceed the fastest for nylon 6, unlike nylon 6,6 in which the condensation reaction proceeds more rapidly. This mechanism difference explains the increased polymerization rates when aminocaproic acid is .



Hydrolysis



Condensation



Addition

Figure 5. Polymerization mechanisms for nylon 6.

added.

After polymerization has occurred approximately 90% nylon 6 is yielded with the remaining containing both non-reacted monomer and also cyclic entities. These are typically extracted using vacuum techniques as well as some additional heating.[28](Twilley)

Morphology/Structure

The morphology of nylon 6 is extremely varied and can take on many different configurations. The molecular orientation of the polymer chains is dependent upon the crystallization conditions, which in turn distinguishes the various phases which they can obtain. Nylons are considered semi-crystalline materials, even in fibers where they obtain high degrees of crystallinity. The melting temperature of nylon 6 is generally reported from 220°C through 228°C as determined by a number of techniques, for example, Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), capillary, and X-ray.[29](Kohan) Nylon 6 can have a broad range of crystallization temperatures and is capable of attaining a high rate of undercooling, sometimes as much as 90°C.[30](Burnett) The high range of temperatures allows the formation of three different crystalline phases in nylon 6. However, the spherulite structure that is observed is always positively birefringent.[31](Kohan)

The two main phases, α and β were discovered in a relatively short time after the first crystallographic determinations of nylon in 1943.[32](Brill) The α phase is the more stable of the two and forms a monoclinic structure in which the chains are aligned in sheets to allow hydrogen bonding. The most accepted crystallographic parameters for the α form are unit dimensions of $a=9.56\text{\AA}$, $b=17.2\text{\AA}$, and $c=8.01\text{\AA}$ (Figure 6).[33](Holmes) Additionally, this monoclinic structure is also capable of changing dimensions in what is termed an α paracrystal structure.[34](Roldan) Unit cell dimensions for this form as determined by x-ray diffraction have ranges equivalent to $a=9.74\text{\AA} - 9.78\text{\AA}$, $b=17.24\text{\AA}$, and $c=8.01\text{\AA} - 8.38\text{\AA}$. This is attributable to

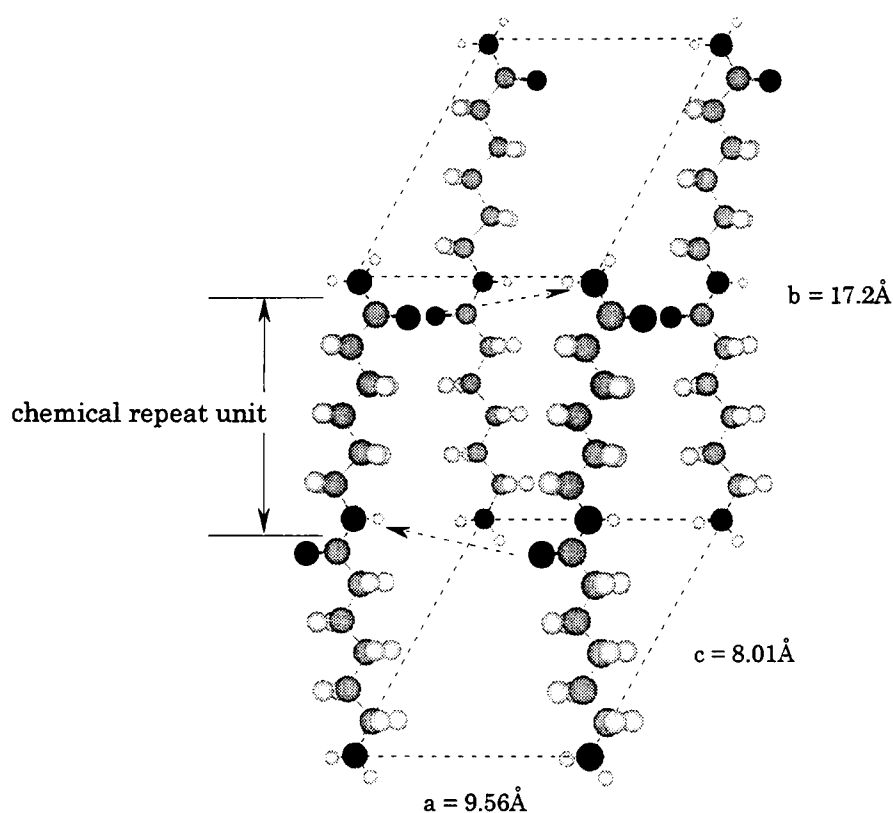
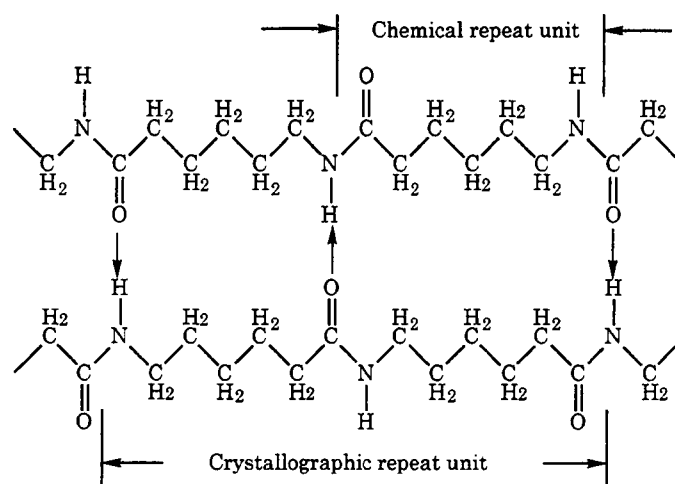
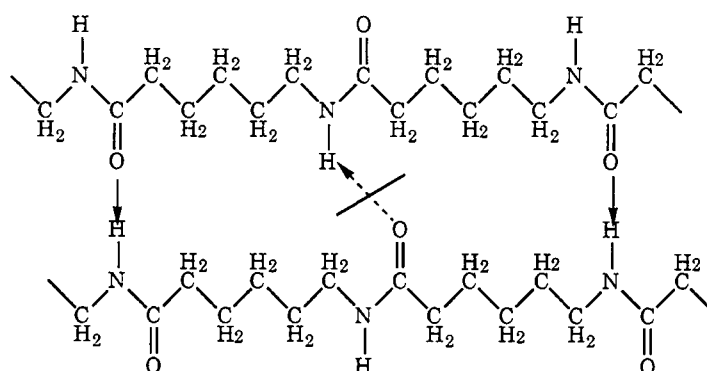


Figure 6. Perspective view of nylon 6 unit cell (α monoclinic).

the lower degree of ordered groups along the chain and a slightly lower amount of hydrogen bonding taking place. This form is usually found in crystalline fibers from the melt in which the heating history is a determining factor of chain spacing dimensions.[34](Roldan) The β form is described as having a hexagonal crystal structure in which the hydrogen bonding forms a type of "network" with its neighbors. This is due primarily to the additional chain twists that are associated with melt oriented fibers.[34](Roldan) It, therefore, can contain both parallel and anti-parallel adjacent chain configurations. Figure 7 illustrates this between two sets of molecular chains.[31](Kohan) The β structure can be formed from a third



Anti-parallel Configuration



Parallel Configuration

Figure 7. Schematic representation of nylon 6 configurations (adapted from Ref. 31.)

phase, the γ pseudo-hexagonal structure, which is the least ordered of the phases. This pseudo-hexagonal phase is essentially an ordered amorphous phase in which there exists a lateral interchain spacing.[34](Roldan) Because there is no real intermolecular order along the main chains, the birefringence of the γ pseudo-hexagonal structure is slightly different than the other phases. The order of

stability for the crystalline structures, therefore, begins with the latter, γ pseudo-hexagonal structure and proceeds through the monoclinic α form.

Plasticization/Degradation

A specific consideration regarding nylon structures is the effect of moisture. Nylon 6 can typically absorb about 2.5 - 3.5 wt. % water under a relative humidity of 70% in the span of 7 days.[35](Weibesch) Maximum saturation limits for water in nylon 6 are 9.5 weight percent.[31](Kohan) This phenomena affects both the actual crystallographic structure and the mechanical properties of the material. Generally, the morphology is not changed, unless the percent crystallinity is initially very low. In the presence of water, the material is able to undergo secondary crystallization. This is due to the plasticizing effect the water has as it interacts with the molecular chains. The water allows a slight rearrangement of the chains on a micromolecular scale, which leads to changes in properties. This plasticization effect on the physical properties is seen even if the water is removed and then replaced.[31](Kohan).

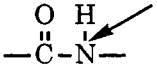
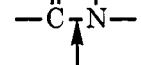
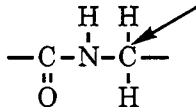
There are a number of mechanisms by which nylon 6 degrades under thermal and chemical influences. Degradation of the material at elevated temperatures is of interest both during processing as well as in service. In general, nylon 6 experiences decomposition above its melting point with the emergence of its formed monomers. The rate of monomer formation is dependent upon a number of variables of which temperature, time, water content, molecular weight, and polymerization residuals all play a part. One published figure for monomer formation is 20-50 moles per 10^6 g/hr @ 250 °C ($H_2O \leq 0.2\%$).[36](Smith) At temperatures 150°- 200°C above the melting temperature, NH_3 , CO_2 , amines, acids,

nitriles and H_2O are formed.[37](Chelnokova) The decomposition mechanism at this point is known to be cleavage of the bonding sites near the amine, however, the exact point at which this occurs is debated.[38-40](Goodman)(Straus)(Kamerbeek) A more detailed description of the various chemical reactions with may occur is presented by Kohan.[31](Kohan)

A similar means for degradation is by thermal oxidation. In this case, however, oxygen diffuses through the material causing chain scission reactions.[41](Neiman) This scission does occur by hydrolytic means, attacking the bond between the nitrogen and carbon atoms, however, it is not as straightforward as simple hydrolysis.[42](Valko) It was also found that these reactions were heightened by the presence of water, most likely acting as a carrier for the oxygen molecule.

Degradation by chemical means is also a consideration for nylon 6. The solvent reactions that can attack the molecular chain are shown in Table 2.[31](Kohan) Some of these reactions can also be desirable effects brought about by careful selection of the solvent.

Table 2. Regions of chemical attack on nylon 6.

Site of chemical attack	Reaction at the site	Result of attack
$-\text{COOH} \ \& \ -\text{NH}_2$	Salt formation, or isocyanate reaction	Eliminates end groups
$\begin{array}{c} \text{O} \quad \text{H} \\ \parallel \quad \\ -\text{C}-\text{N}- \end{array}$ 	Alkoxyalkylation	Lowers crystallinity, facilitates crosslinking
$\begin{array}{c} \text{O} \quad \text{H} \\ \parallel \quad \\ -\text{C}-\text{N}- \end{array}$ 	Hydrolysis	Formation of intermediates
$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{N}-\text{C}- \\ \parallel \quad \\ \text{O} \quad \text{H} \end{array}$ 	Irradiation in the presence of monomer	Chain grafting

The ability for the chemical solvent to attack nylon is dependent upon how easily it can diffuse throughout the material. Therefore, the plasticizing effect it has on the molecular structure greatly changes its ability to react at the designated sites. So, factors that would influence this ability include crystallinity, water content, and temperature.[43](Weiske)

Filler Materials

Calcium Chloride (CaCl_2)

Calcium chloride is typically not utilized as a particulate filler material for composites. It does maintain a stable deformed rutile crystal structure ($a=6.24\text{\AA}$, $b=6.43\text{\AA}$, $c=4.20\text{\AA}$), but only under low humidity conditions.[44](van Bever) Because it is highly hygroscopic, it is typically used in aqueous mediums. For instance, the largest calcium chloride market is that of cement, mainly for concrete production purposes. In this application the disassociated ions in solution act as binding/attraction agents for the particulates in that medium. Discussions on polymer specific applications with CaCl_2 will be presented later.

Hydroxyapatite (HA)

Hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) is a phosphate based calcium salt which constitutes the particulate filler for human bone. The unit cell dimensions of the hexagonal rhombic structure it forms are $a=9.432\text{\AA}$ and $c=6.881\text{\AA}$. [45](Posner) This crystalline material is highly insoluble, having a solubility parameter, K , of 10^{-59} . [46](Boskey) This insolubility makes the material ideal for the natural reinforcement of the collagen matrix, or as artificial coatings for implants. If it were

used strictly as a particulate filler HA has an appropriately high elastic modulus, approximately 117 GPa for the synthetic material and 144 GPa as found in bone.[7](Grenoble) The natural composite structure it forms with collagen will be discussed later.

Blend Systems

Due to the demanding requirements on today's polymer materials, ways in which to improve particularly weak properties are always being sought after. This is typically accomplished by blending two or more materials to arrive at the desired properties. This process of blending can be carried out a number ways, be it physical mixing of particulates, molten-state mixing, solution mixing, grafted polymer systems, etc. Although not all of these particular methods lead to complete mixing, or even actual bonding between the system's components, they usually lead to some physical interaction which will alter the singular component's original properties.

Particulate Blends

Particulate blends, or filled polymer blends are considered a type of composite material. Instead of the second phase being a continuous fiber, as in carbon fiber composites, or short discontinuous fibers as in most glass fiber reinforced composites, it is a particulate. The particles themselves can be any number of different materials, organic, inorganic, etc., with properties that are typically different than the matrix. Certain advantages that are sought with filled polymer systems are given below.[47](Nielsen)

- a. To stiffen the matrix and make it rigid
- b. To regulate the coefficient of thermal expansion
- c. To improve heat resistance
- d. To reduce creep
- e. To increase the strength
- f. To modify permeability to gases and liquids
- g. To improve electrical properties
- h. To modify rheological properties
- i. To lower the cost of the material

One example of a physical blend, or immiscible composite, is polystyrene and rubber. This material is composed of a matrix of polystyrene, a glassy, low impact resistant polymer and rubber, *cis*-1,4 polybutadiene. There exists a low degree of compatibility of the materials with each other, and hence, a moderate degree of improved properties. In this particular case, the rubber acts as craze stopping points, which leads to a higher final elongation as well as increased overall toughness of the material.[48](Deanin)

In order to further increase the effect of an additional phase, compatibilizing agents are sometimes used. These materials attempt to create an interface between the particles and the surrounding matrix. By using nylon 6 and rubber particles as an example, the addition of a cross-linked elastomer to this two-phase system increased impact as well as tensile elongation.[49](Chompff) This now three-phase system shows the effect of increased interfacial adhesion of the rubber particles to the nylon 6 matrix.

Nylon/Salt Blends

A great deal of work has been done on the effects of inorganic salts on polyamides, in particular Nylon 6 and Nylon 6,6. Valenti et al. studied the changes in physical and chemical properties resulting from the addition of lithium chloride (LiCl) and lithium bromide (LiBr).[50][51](Valenti, Bianchi) These investigators

noted several changes at salt concentrations below 4% by weight. In particular, LiCl and LiBr dissolved in the polymer produced a decrease in the melting temperature and the rate of crystallization. Other studies utilizing the same system showed that both salts also lead to an increase in the melt viscosity and glass transition temperature as measured by differential scanning calorimetry.[52][53](Acierno) These effects have been attributed to a strong interaction between the amide carbonyl groups in the amorphous polymer phase and the lithium cations.[54](Valenti) The morphological alteration due to addition of lithium salts has been used to induce higher amorphous orientation in spin-drawn fibers, which leads to a higher modulus.[55](LaMantia)

Other salts have also been used to alter the physical properties of Nylon 6. Siegmann and Baraam used copper chloride to produce melting point depression and retardation of the crystallization rate.[56](Siegmann) Szafner and Karger-Kocsis added chromium III ions to produce an increase in melt viscosity and amorphous content.[57](Szafner) The changes in properties that are observed with copper chloride and chromium III ions are similar to those observed for the lithium salts. These changes are also attributed to a strong interaction between the amide carbonyl group and the cation, which leads to a disruption of the crystalline structure and a subsequent observed decrease in melt temperature. The interaction may persist in the molten state leading to an increase in melt viscosity.

Theoretical Property Determinations of Blends

The increasing use of blends and composites requires that a system of theoretical formulations be created to quantify the resultant properties. There exist

a number of theories for determining properties of filled polymers. Due to both technological advances (computers) as well as the sheer number of systems to study, there have been improvements over Einstein's first theories of reinforced matrices.

Equations for Moduli

From a simple model of an aggregate dispersed in a matrix, Einstein developed an expression for the shear modulus, G , of the composite (matrix/filler) as a function of filler weight fraction, ϕ_2 . [58](Einstein) In all of the following equations, the subscript 1 refers to the matrix and 2 to the filler material.

$$G = G_1(1 + 2.5\phi_2) \quad (1)$$

This formula assumes that filler particles and matrix are bonded securely with not slip between them. Equation 2 takes into account slipping between the phases and hence, results in a lower contribution of the filler to the reduced modulus, G/G_1 . [58](Einstein)

$$G = G_1(1 + \phi_2) \quad (2)$$

A small modification to the initial principle was postulated by Eilers-Van Dijk to account for the effective volume of the filler. The constant V in the following equation is equivalent to the ratio of the sedimentation volume of the filler relative to the true volume of the filler. [59](Eilers)

$$G/G_1 = \left\{ 1 + \left[1.25\phi_2 / (1 - V\phi_2) \right] \right\}^2 \quad (3)$$

An additional modification to Einstein's original theory is presented for rubber spheres in a matrix. [60][61](Guth)(Smallwood)

$$G = G_1(1 + 2.5\phi_2 + 14.1\phi_2^2) \quad (4)$$

The increase in modulus is slightly higher than that for a non-slipping Einstein system.

However, the aforementioned equations have their limitations when used to predict the shear modulus over the entire range of filler concentrations. Einstein's equation is not valid because it cannot predict the inversion of filler and matrix concentrations. The same problem exists for the theories postulated by Guth and Smallwood and Eilers-Van Dijk in which the modulus prediction is greater than that of the experimental values.[47](Nielsen)

Unlike the previous theories, Kerner developed an expression to evaluate the filler material's contribution over the entire range of the two phase system. The following equation also allows for variances in the order of degree by which the filler material's modulus exceeds that of the matrix.[62](Kerner)

$$G = G_1 \left[\frac{\frac{\phi_2 G_2}{(7-5\nu_1)G_1 + (8-10\nu_1)G_2} + \frac{\phi_1}{15(1-\nu_1)}}{\frac{\phi_2 G_1}{(7-5\nu_1)G_1 + (8-10\nu_1)G_2} + \frac{\phi_1}{15(1-\nu_1)}} \right] \quad (5)$$

If the values of the moduli between matrix and filler are vastly different this equation will reduce to simpler form, with only the value of ϕ and ν (Poisson's ratio) being included.

Further work on these and other shear modulus theories was performed by Halpin and Tsai who developed an equation that is applicable to all elastic moduli. Their formulation allows for shear, Young's or bulk moduli and is defined as the following:

$$M = M_1 \left[\frac{1 + AB\phi_2}{1 - B\phi_2} \right] \quad (6)$$

where M is the modulus and A and B are constants.[63][64](Tsai)(Halpin) A is a geometric constant accounting for particles that are not necessarily spherical. The

constant, B , is a factor of the relationship between the filler and matrix moduli and is given as

$$B = \frac{(M_2/M_1) - 1}{(M_2/M_1) + A} \quad (7)$$

The application of these equations is valid for most rigid systems, however, it neglects certain considerations required for a viscous matrix.[65](Nielsen) To account for the changes due to possible filler agglomeration, or sedimentation, an effective packing fraction term must be incorporated.[66](Mooney) Therefore, the final equation becomes one in which a modified Poisson's ratio is accounted for in k as well as the value for viscous considerations, ψ . [65](Nielsen)

$$M = M_1 \left[\frac{1 + (k-1)B\phi_2}{(1 - B\psi\phi_2)} \right] \quad (8)$$

The value of k is a relative Einstein's coefficient which is determined from the relationship of Poisson's ratio to that of the effective particle geometry. A list of these relative values is given in Table 3.[65](Nielsen)

Table 3. Relative Einstein coefficients for various Poisson ratios.

Poisson's ratio, ν_I	Ratio of k at ν_I / k at $\nu_I = 0.5$
0.5	1.00
0.4	0.90
0.35	0.867
0.3	0.84
0.2	0.80

In the event that there is lack of cohesion between the matrix and the particulate filler, as with Equation 2 the Einstein "slippage" theory, Sato and Furukawa considered the resulting voids around the particles.[67](Sato) This

“cavitation” is detrimental to the overall modulus and the prediction is expressed in terms of an adhesion factor, or cavitation fraction. The following equation was developed for this case

$$E = E_1 \left[\left\{ 1 + \frac{1}{2} \frac{y^2}{1-y} \right\} \left\{ 1 - \frac{y^3 T}{3} \left(\frac{1+y-y^2}{1-y+y^2} \right) \right\} - \frac{y^2 T}{3(1-y)} \left(\frac{1+y-y^2}{1-y+y^2} \right) \right] \quad (9)$$

where T is the adhesion factor and $y = \phi_2^{1/3}$. Cavitation, therefore, occurs when T has a value of zero, and perfect adhesion is when $T=1$.

To compare the relative effectiveness of predicting an actual polymer system data acquired by Lewis and Nielsen will be used.[68](Lewis) A rigid epoxy matrix having a Poisson's ratio of 0.35 is given as well as the maximum packing fraction, ϕ_m . Figure 8 contains the results for these calculations using all of the aforementioned theories, since they are all applicable for reduced shear moduli. It appears that the Nielsen, Guth & Smallwood, and Tsai-Halpin equation predict the experimental results within acceptable error. The deviations from experimental results increase, however, at concentrations of filler near and above 50%. The Tsai-Halpin equation yields a similar prediction to the Nielsen for this case because the viscous matrix factor, ψ , is negligible for this system in which the matrix is rigid. Lewis and Nielsen, therefore, tested Nielsen's prediction in a liquid matrix to show the global application of the equation and the shortcomings of the Tsai-Halpin equation.[68](Lewis)

Equations for Tensile Properties

The effect of particle fillers on the tensile properties of polymers is a misunderstood subject. Adding small particulates usually has a two fold result. The modulus of a filled system is known to increase with the increase of volume fraction

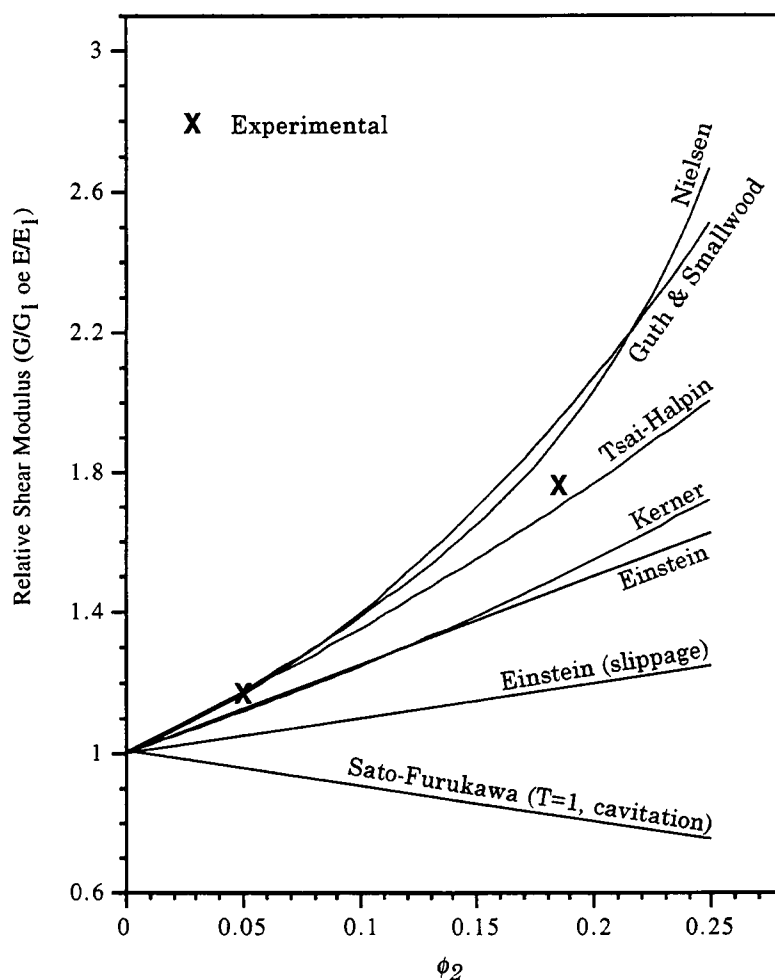


Figure 8. Comparison of theoretical shear moduli equations.

filler, but this is not always the case with the tensile strength. It has been observed that an increase in the actual density of the material is a contributing factor to increased tensile properties. This may be brought about by increased crystallization of the matrix, or simply by the nature of denser particles being incorporated into the original material. Following these basic principles then, the tensile strength of a filled system can be approximated with the following equation

$$\sigma_B = \sigma_{B0} e^{-aP} \quad (10)$$

where σ_B is the strength of the composite, σ_{B0} is the strength of the material without porosity and P is the volume fraction of voids created by the filler.[69](Passmore) At relatively high porosity, therefore, the tensile properties are reduced due to the loss of adhesion between the matrix and the filler. This phenomena has been termed dewetting, which can also be attributed to breakup of the filler particles.[70](Bryant) The increase in dewetting results in a reduced elongation and lower tensile strength due to the voids acting as crack initiation sites. This same line of thought applies to Kerner's model for tensile strength.[62](Kerner) The tensile strength is deteriorated as the crack progresses from one void space to another. Additionally the equation accounts for the stress concentrations that may be introduced due to the particles in the polymer matrix. This formulation is shown as

$$\frac{\sigma_{B(filled)}}{\sigma_{B(unfilled)}} = (1 - \phi_2^{2/3})S \quad (11)$$

with S being the concentration factor. A value of 1.0 would indicate that no concentration effects are evident.

An attempt to predict the elongation to break based upon these same principles has been presented by Nielsen. The proposed model assumes perfect adhesion between spherical particles within the matrix. The formulation is shown in Equation 11.[71](Nielsen)

$$\frac{\epsilon_{B(filled)}}{\epsilon_{B(unfilled)}} = 1 - \phi_2^{1/3} \quad (12)$$

The effect of small amounts of filler particles on the elongation to break is dramatic due to the assumption of good particle/matrix adhesion. There also exists the assumption that the polymer is breaking at the same elongation as that of the

unfilled polymer, making the above equation a relative comparison of the two systems.

In order to apply the theory of elongation to break into an impact strength, or "toughness" determination it is necessary to incorporate the theoretical models for modulus. A major assumption in combining these models is that the polymer matrix is rigid and exhibits a linear, or Hookean stress-strain curve. If this is indeed the case of the filled polymer, the impact strength can therefore be assessed by [71] (Nielsen)

$$\text{Impact strength} = \sigma_B \varepsilon_B / 2 = E \varepsilon_B^2 / 2 \quad (13)$$

A plot illustrating the theoretical predictions using the Kerner and Eilers-Van Dijk equations are shown in Figure 9. [71] (Nielsen)

Both theoretical predictions for impact strength expect a drastic decrease with the inclusion of even small amount of filler. This is known to not be the case in a system such as toughened polystyrene in which rubber particles make a significant improvement in properties. There exists, therefore, room for improvement when dealing with factors such as particle adhesion, crystallinity, and the existence of crack energy formation, especially in calculated properties such as impact strength.

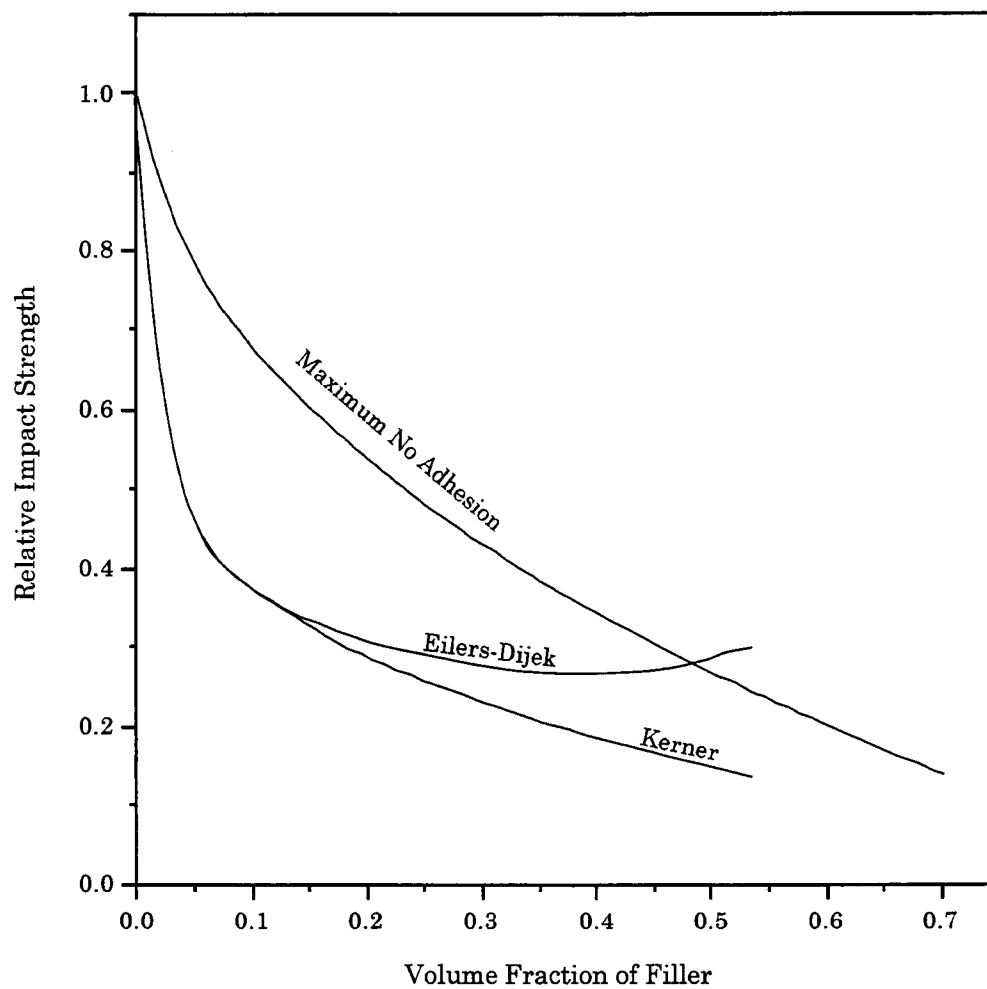


Figure 9. Theoretical prediction for impact strength of filled polymers

CHAPTER II

EXPERIMENTAL

Materials

The polyamide used in this study was polycaprolactam produced by Allied Signal. The weight average molecular weight of this polymer was approximately 28,000. The resin as received was specified as nylon 6 for use in fiber production. The calcium chloride used was supplied by Mallinckrodt as analytical grade pellets of mesh 4-20 and $\rho=2.512 \text{ g/cm}^3$. The pellets were further reduced in size (to approximately 6-12 microns) using a mortar and pestle to facilitate dispersion. The calcium phosphate salt, or synthetic hydroxyapatite was supplied in powdered form by Fisher Scientific Co., with a density of 3.019 g/cm^3 and an average particulate size of 0.5-2.0 microns.

Blends - Formation and Processing

Hammermill Blending

The mechanical mixing of the nylon 6 with the particulate salt blends was facilitated with the use of a Raymond Hammermill grinder. The nylon was ground after being immersed in liquid nitrogen to ensure no thermal degradation from the grinding process. A schematic of the grinder is shown in Figure 8. After a sufficient amount of nylon was processed, approximately 10 pounds, each salt was blended

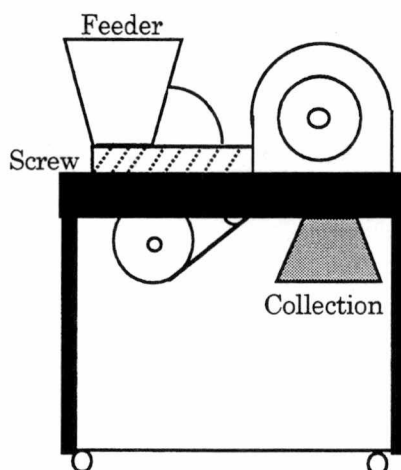


Figure 10. Schematic of the Hammermill mechanical grinder.

into the material by rolling the mixture for 2 hours. The resulting compositions for each blend were approximately 0.5, 1.0, 5.0, 6.0, and 10.0 weight percent salt.

Solution Mixing

Solutions of nylon 6 were prepared using acetic acid as the solvent. The ratio of polymer to solution was 10 grams of nylon per 40 ml of acetic acid glacial (99% pure). To facilitate the dissolving of the nylon the solvent was heated almost to the point of boiling, or approximately 110°C. This solution was left to mix under these conditions for 1.25 hours, or until all of the nylon was dissolved. Care was taken to ensure the material was not left for an extensive amount of time as the acetic acid will break down the polymer.

After complete solutionizing, the appropriate amount of calcium salt or hydroxyapatite was added to a separate beaker containing heated acetic acid before being introduced into the polymer/solvent solution. In this manner it was possible to create calcium chloride solutions up to 6.0 weight percent salt.

This mixture was then left to stand at room temperature under a laboratory hood for 48 hours to allow the polymer to cool and for excess solvent to evaporate. The compound was then placed in a vacuum oven at 80°C for 48 hours to remove the remaining solvent. A "trap" consisting of a glass collection tube in dry ice was established to collect the solvent as it was drawn off by the vacuum pump.

Sample Preparation

Melt Pressed Thin Films

Thin film samples were prepared from each of the two blending techniques via a melt pressing technique. A small amount of polymer blend was placed on an aluminum plate between Teflon® sheets, which were then placed between the steel platens of a Wabash melt press at a temperature of 250°C. To avoid plastic flow of the Teflon® sheets, the material was placed on the lower platen and raised until almost touching the upper platen. The polymer blend was then left to melt for 4 minutes at which point a light piece of aluminum plate was placed on top of the Teflon® sheets. At this time pressure was gradually applied until a maximum of approximately 18 MPa (5 tons/4 in² on the Wabash indicator).

The samples were removed from the press and left to cool to room temperature, an effective rate of 100°C/min., immediately after which they were placed in a dessicator to assure a dry environment. Samples marked for conditioning to room humidity were also placed in the dessicator until needed. The "wet" samples were prepared in an approximate humidity of 60% at a temperature of 22°C for 96 hours. Samples pressed from both powder and solution were used in

tensile measurements whereas only solution prepared material was utilized for dynamic testing.

Injection Molded Samples

Molded specimens for use in x-ray diffraction, tensile tests, and attenuated total reflectance (ATR) spectroscopy were prepared via a tabletop injection molding system. A small-scale, air driven injection molder from was used in conjunction with a series of heating elements to produce the desired samples (Figure 11).

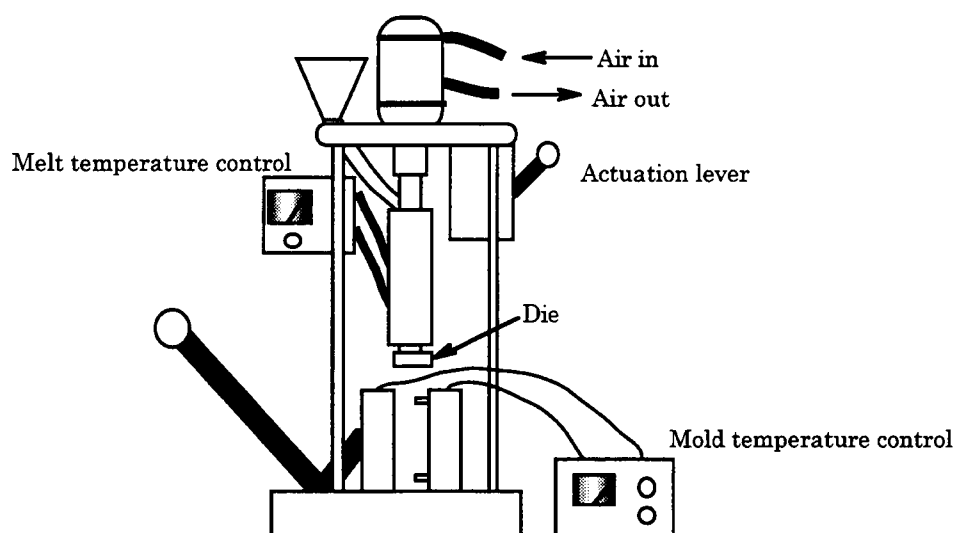


Figure 11. Table-top injection molder system.

The specimen mold used for use in the tensile tests had the following “dogbone” dimensions:

Narrow section width	7.0 mm
Narrow section thickness	3.21 mm
Overall width	19.0 mm
Overall length	114 mm

The impact specimen mold had dimensions of $63.2\text{mm} \times 13.3\text{mm} \times 6.01\text{mm}$.

The solution prepared samples were hand pulverized into small enough pieces (the largest being $3\text{ cm} \times 5\text{ cm}$) to fit into the barrel. The material was loaded manually as the automatic feeder was unable to accommodate the awkward material sizes. The mold temperature was set at 85°C and maintained throughout the process. Injection pressure was held constant using a compressed air/regulator system separate from the engineering building supply. This allowed an adequate pressure of 110 psi to be maintained constantly.

Polarized Light Microscopy (PLM) Samples

Microscopy samples were prepared using a razor blade and a secure cutting surface. Each composition was carefully sliced as thin as possible from the dried solution material. This was then placed between a standard glass slide and coverslip.

Differential Scanning Calorimetry (DSC) Samples

Utilizing a similar method to that of PLM, the half of the calorimetric samples were prepared from the dried solution material. Approximately 5 mg of material was sectioned from the center of the dried solution. In addition, samples were removed from the injection molded pieces near the surface. This was then placed in a standardized aluminum pan, covered with a lid and crimped using a Perkin-Elmer press.

To elucidate certain thermal characteristics that were observed during experimentation, additional concentrations of only the CaCl_2 salt blends were

prepared. Weight percent concentrations of 2.0%, 3.0%, and 4.0% were added to the previous concentrations for a total of seven CaCl_2 salt blends.

One additional blend was also prepared for specific analysis in the differential scanning calorimeter. In order to determine the possible existence of a nucleating agent in the supplied polymer resin, a purification process was employed. An acetic acid solution was prepared with 50 ml of solvent and 10 grams of polyamide. This was heated until complete dissolution had taken place. 500ml of acetone were prepared as the polar solvent to precipitate out the nylon. The dielectric constants of the protic solvent, acetic acid, and that of the aprotic solvent, acetone, are 6.1 and 21 respectively.[72](Carey)

Fourier Transform Infrared (FT-IR) Spectroscopy Samples

The thin film requirements for FT-IR were met by using a hot plate to melt the blends. The solution prepared material was sliced into a small piece and placed upon a Teflon® sheet and then placed on the hot plate. A second piece of Teflon® was placed over the first and then pressed, by "hand", until an appropriately small film was obtained. This method required more care as the temperature of the hot plate was not readily obtained.

Injection molded samples were studied using an FT-IR attenuated total reflection (ATR) technique. The ATR technique does not need a significant amount of sample preparation other than requiring two flat sample surfaces. Care was taken to ensure that each crystal was secured and in full contact with the specimen.

Tensile Testing

Instron Table Model

To test the thin film materials an Instron table top model 1122 tester was used. This was computer controlled via a Gateway™ 486 PC with Instron® software. The model was calibrated to a 9.8 Kgf scale in accordance to ASTM standard D882-90 for thin films. Sample dimensions were 4mm in width by ~0.16mm (± 0.04) in thickness with a gage length of 20mm. A crosshead speed of 50 mm/min. was chosen based upon trial runs of pure materials as well as recommendations from the ASTM standard. Six samples of each composition, "wet" and dry, were tested resulting in four "average" samples for actual calculations.

Phoenix Floor Model

Injection molded tensile specimens were tested on a Phoenix 20 kip load frame. This was controlled with a PC and testing software provided by MTI (Measurements Technology Inc.). The ASTM standard for tensile properties of plastics, D638-91 was used as a guide in sample preparation. The initial dimensions of the test specimens were 7.46mm (± 0.18) in width by 3.34mm (± 0.14) thick. Crosshead speed for the thick specimens was the same as that for thin samples, or 50 mm/min. with the gage length at 35mm. A series of five samples were pulled for each composition, "wet" and dry, with the three most consistent being chosen for calculations.

For both tensile tests the material property calculations were the same. The values of maximum tensile stress (σ), maximum strain (%), and Young's modulus (E) were calculated according to the following:

$$\sigma_{uts} = \frac{\text{Maximum load } (P_{\max})}{\text{Initial cross-sectional area } (t_o \times w_o)} \quad (14)$$

$$\text{Strain}(\%) = \frac{\text{Final length } (L_f)}{\text{Initial length } (L_o)} \times 100 \quad (15)$$

$$E = \frac{\Delta\sigma}{\Delta\epsilon} \text{ (of elastic region)} \quad (16)$$

The resulting experimental values were compared to theoretical predictions for all three mechanical properties, tensile stress, strain, and modulus. A particular prediction was chosen for each system (CaCl_2 or hydroxyapatite) based upon the trends observed, for example, increasing, or decreasing changes in modulus, or strength with increase in salt concentration. Those theories that presented the "best fit" for each set of data are shown below:

Reduced modulus - Sato-Furukawa prediction

$$E/E_1 = \left[\left\{ 1 + \frac{1}{2} \frac{y^2}{1-y} \right\} \left\{ 1 - \frac{y^3 T}{3} \left(\frac{1+y-y^2}{1-y+y^2} \right) \right\} - \frac{y^2 T}{3(1-y)} \left(\frac{1+y-y^2}{1-y+y^2} \right) \right] \quad (17)$$

Tensile Stress - Kerner prediction

$$\frac{\sigma_B(\text{filled})}{\sigma_B(\text{unfilled})} = (1 - \phi_2^{2/3})S \quad (18)$$

Tensile Stress - Passmore prediction

$$\sigma_B = \sigma_{B0} e^{-aP} \quad (19)$$

Breaking Strain - Nielsen prediction

$$\frac{\epsilon_{B(\text{filled})}}{\epsilon_{B(\text{unfilled})}} = 1 - \phi_2^{1/3} \quad (20)$$

Differential Scanning Calorimetry

Thermoanalytical measurements were performed using a Perkin Elmer model DSC-7 differential scanning calorimeter. Exothermic and endothermic curves were obtained utilizing Perkin Elmer TAS-7 software running in UNIX on a Digital Equipment Corporation 486 PC. The temperature profiles for all samples were the same and are outlined in Table 4.

Table 4. DSC heating parameters.

Parameter	Value
Starting temperature	60°C
Heating rate	20°C/min.
Maximum temperature	260°C
Cooling rate	20°C/min.
Final temperature	60°C

The above thermal treatment was performed twice in succession on the solution cast samples to erase their prior crystallization history.

The nature of the salt/polymer matrix allows a theoretical prediction as to the changes in melting temperature as a function of concentration. The basis for this is outlined in Flory, which relates the enthalpy of crystalline units to the effects of a diluent, or incorporated phase.[73](Flory) The depression, therefore, is estimated based upon the well know equation

$$(1/T_m) - (1/T_m^0) = (R/\Delta H_u)X(v_1 - v_1^2\chi_1) \quad (21)$$

where T_m^0 is the melting temperature of the pure material, ΔH_u is the melting enthalpy for a unit of crystallizable polymer, X is the ratio of molar volumes of the polymer and diluent, v_1 is diluent volume fraction, and χ_1 is an interaction

parameter.[73](Flory) The melting enthalpy in this case is taken as 5100 cal/mol with an interaction parameter of 0.2, which is a reasonable estimate based upon the literature.[74](Dole) The molar volume for the CaCl_2 salt is calculated as 7.34.

Crystallinity calculations were performed using the standard enthalpy ratio equation given as

$$\% \text{Crystallinity} = \frac{\Delta H_{\text{measured}}}{\Delta H_o(\text{ideal crystal})} \times 100 \quad (22)$$

with the ideal ΔH equivalent to 45 cal/g, or 188.3 J/g.[75](Liberti)

Wide angle X-ray Diffraction

Crystallographic determinations were performed on a Rigaku Geigerflex X-ray spectrometer. Using a $\text{Cu K}\alpha$ source, the instrument was run in reflectance mode due to the thickness of the injection molded samples. The spectrum was collected between the 2θ angles of 7 and 35 degrees. The time constant and scale counts were adjusted so as to permit accurate determination of the peak positions.

Analysis of peak position as well as peak area was accomplished with the help of the software package, PeakFit for DOS compatible computers. This allowed peak area "fits" to be performed to elucidate the total area from a particular morphological structure, i.e., a specific crystalline phase. The Gaussian and Pearson curve-fitting equations used for this analysis are

$$\text{Gaussian equation} \quad a_o \exp \left[-0.5 \left(\frac{x - a_1}{a_2} \right)^2 \right] \quad (23)$$

$$\text{Pearson equation} \quad \frac{a_o}{\left[1 + 4 \left(\frac{x - a_1}{a_2} \right)^2 \left(2^{1/a_3} - 1 \right) \right]^{a_3}} \quad (24)$$

with a_0 the amplitude, a_1 the peak center, a_2 and a_3 the peak widths. The second peak width parameter in the Pearson equation permits a "sharper" peak to be defined compared to that of the Gaussian fit. The equations, therefore, were applied appropriately, utilizing a Gaussian equation for the amorphous areas and the Pearson equation for the crystalline peaks. For an accurate analysis the data set size for the x-ray spectrums numbered more than 500 points.

Fourier Transform Infrared Spectroscopy

Molecular vibrational spectroscopy was performed using a Digilab FTS-40 Fourier Transform infrared spectrometer. Scans were performed in both a transmittance (converted to absorbance) and an attenuated total reflectance (ATR) mode. Spectrum acquisitions in transmittance were collected with 256 scans at a resolution of 4 cm^{-1} . The thin film samples were those pressed on the hot plate as described previously. The resulting spectrums were subsequently converted to absorbance via the supplied Bio-Rad software.

To effectively resolve the changes in the motions of the carbonyl groups, both Fourier deconvolution and differentiation methods were employed. Deconvolution was performed first to determine existing peaks and their positions. Once noted, differentiation of the carbonyl region (1740cm^{-1} - 1560cm^{-1}) was performed. The parameters for these methods are shown below:

Deconvolution		
Half bandwidth	16	
"K" factor	1.7	
Apodization	Bessel	
Differentiation		
Differentiation order	2	
Passband edge	0.17	

The descriptions of these techniques can be found in the Bio-Rad Fourier Manipulations owner's manual (part # 091-0466)[76](Bio-Rad)

ATR spectrums were collected as the sum of 64 scans performed at a resolution of 4 cm^{-1} . The reflectance apparatus was a continuously variable ATR #301 supplied from Spectra Tech. A KRS-5 internal reflectance crystal was used that had dimensions of $1\text{cm} \times 5\text{cm}$ and a refractive index (η) of 2.38'. The incident beam angle used was 60° with an internal reflection angle of 45° , creating an effective maximum penetration of 1 micron.

Dynamic Mechanical Analysis

Mechanical relaxation spectroscopy was collected on a Dynamic Viscoelastometer from IMASS Co., Connecticut. The system was composed of a Toyo Baldwin Rheovibron mechanical tester connected to an Autovibron spectrometer housed with a Hewlett Packard model 6940B Multiprogrammer. Additionally, a Hewlett Packard computer (model 9816) running HP Basic controlled the hardware and the collection of data. All samples were subjected to three vibrational frequencies, 1.1, 11, and 110 Hz, over a temperature range of -150° to 250°C . The temperature ramp was 2 degrees Celsius/minute with an error of ± 2 degrees. The 11 Hz frequency was used for most of the data analysis.

Notched Izod Impact

Impact studies for the polyamide blends were conducted utilizing a Tinius-Olson Charpy/Izod impact tester. This machine was capable of being suited for

either task. In Izod mode, the plastic is inserted as a beam, with the notch in this case faced towards the striking edge. The pendulum head and release height were in accordance with ASTM standard D 256 for impact resistance of plastics and electrical insulation materials.

Theoretical predictions for impact strength are derived from the aforementioned Kerner equation in which the impact strength for his model was calculated based upon

$$\text{Impact strength} = \sigma_B \epsilon_B / 2 = E \epsilon_B^2 / 2 \quad (25)$$

and is entered into the following equation:

$$\frac{\text{Impact strength (filled)}}{\text{Impact strength (unfilled)}} = (1 - \phi_2^{2/3})S \quad (26)$$

Polarized Light Microscopy

Morphological observation was performed with the use of a polarized light microscopy setup. The setup consisted of an Olympus BF22 light microscope connected to a video capture system which is shown in Figure 12. A Mettler FP-80 hot stage provided the thermal conditions which were captured with a video system consisting of a Panasonic video camera connected to a Sony 12" color display and a JVC video recorder.

This configuration allowed real-time recording of the crystallization and/or melting of the samples for accurate analysis. The timer facilitates the measurement of spherulitic growth in the polymer being studied. Cooling rates slower than 20°C/min. were experimented with to try and acquire reasonable images. This also included "isothermal" crystallization near the crystallization point as determined by

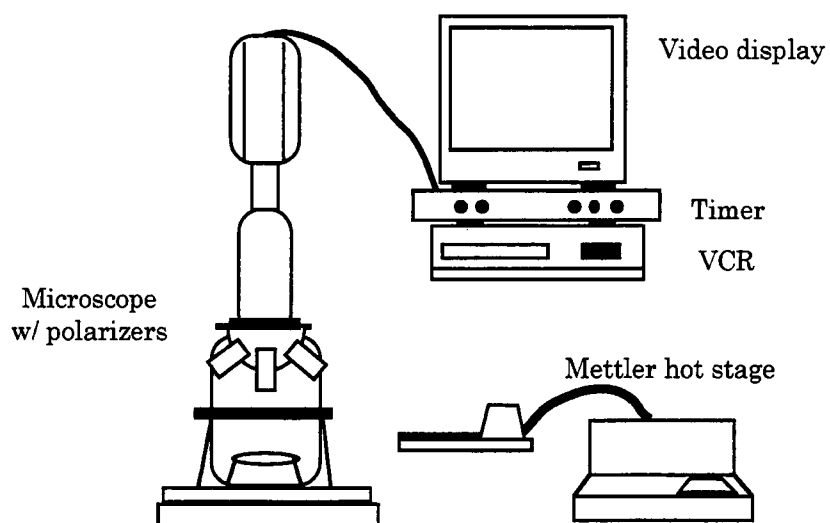


Figure 12. Polarized light microscopy setup.

the DSC. In most cases this was 180°C and required approximately 30 minutes to complete the crystallization process.

CHAPTER III

RESULTS

Based upon preliminary tensile property findings the following is data acquired from the solution prepared method only. The powder-formed materials all had voids incorporated into each sample due to the fact that none of the particulate salts that were mixed with the materials were incorporated into the matrix. Subsequently, the particles acted as crack initiation sites and formed large agglomerates throughout the samples, which removed the possibility of being a viable material option.

Tensile Testing

Injection Molded Specimens

The results of the injection molded uniaxial tensile tests for all concentrations of blends are listed in Tables 5 and 6. Samples of as-received pellets and pure solution molded specimens are also included. Example plots for the "average", or representative curves of each blend are shown in Figures 13 through 16. The accompanying physical property values are presented in Tables 5 and 6. Plots depicting the changes in physical properties with the changes in concentration are shown in Figures 17 through 22. These also contain the appropriate theoretical predictions from the various previously mentioned references.

Table 5. Tensile properties of dry, molded samples.

Material	E (GPa)	$\sigma_{\max}$ (MPa)	Strain (%)
n6peldry - Dry as-received	1.35 ± 0.094	86.2 ± 3.45	60.4 ± 6.90
n6soldry - Dry from solution	1.63 ± 0.038	74.8 ± 3.54	22.0 ± 0.42
n601HAdry - 1.0% HA dry	1.58 ± 0.153	48.0 ± 4.36	3.65 ± 0.83
n650HAdry - 5.0% HA dry	1.56 ± 0.165	41.3 ± 11.1	2.85 ± 0.68
n660HAdry - 6.0% HA dry	1.62 ± 0.139	38.7 ± 3.51	3.05 ± 0.49
n610HAdry - 10.0% HA dry	1.49 ± 0.164	37.1 ± 4.35	3.59 ± 0.35
n605Cl dry - 0.5% CaCl ₂ dry	1.48 ± 0.091	88.0 ± 10.7	39.1 ± 0.70
n601Cl dry - 1.0% CaCl ₂ dry	1.53 ± 0.032	86.5 ± 2.96	18.1 ± 1.67
n650Cl dry - 5.0% CaCl ₂ dry	1.40 ± 0.125	79.3 ± 11.5	6.77 ± 0.42
n660Cl dry - 6.0% CaCl ₂ dry	1.51 ± 0.108	38.6 ± 3.31	4.35 ± 1.18

Table 6. Tensile properties of conditioned, molded samples.

Material	E (GPa)	$\sigma_{\max}$ (MPa)	Strain (%)
n6pelwet - Wet as-received	1.57 ± 0.096	78.1 ± 2.03	117 ± 49.6
n6solwet - Wet from solution	1.42 ± 0.211	74.0 ± 7.77	44.8 ± 20.5
n601HAWet - 1.0% HA wet	1.43 ± 0.192	45.1 ± 8.64	6.08 ± 1.25
n650HAWet - 5.0% HA wet	1.42 ± 0.151	39.5 ± 7.71	4.17 ± 1.14
n660HAWet - 6.0% HA wet	1.26 ± 0.148	36.0 ± 7.65	3.48 ± 0.62
n610HAWet - 10.0% HA wet	1.17 ± 0.169	34.4 ± 3.95	3.45 ± 0.58
n605Clwet - 0.5% CaCl ₂ wet	1.52 ± 0.668	78.3 ± 2.20	35.2 ± 11.9
n601Clwet - 1.0% CaCl ₂ wet	1.37 ± 0.075	77.5 ± 1.71	22.0 ± 2.33
n650Clwet - 5.0% CaCl ₂ wet	1.38 ± 0.081	84.3 ± 0.71	11.4 ± 1.95
n660Clwet - 6.0% CaCl ₂ wet	1.36 ± 0.052	68.3 ± 5.75	7.56 ± 1.64

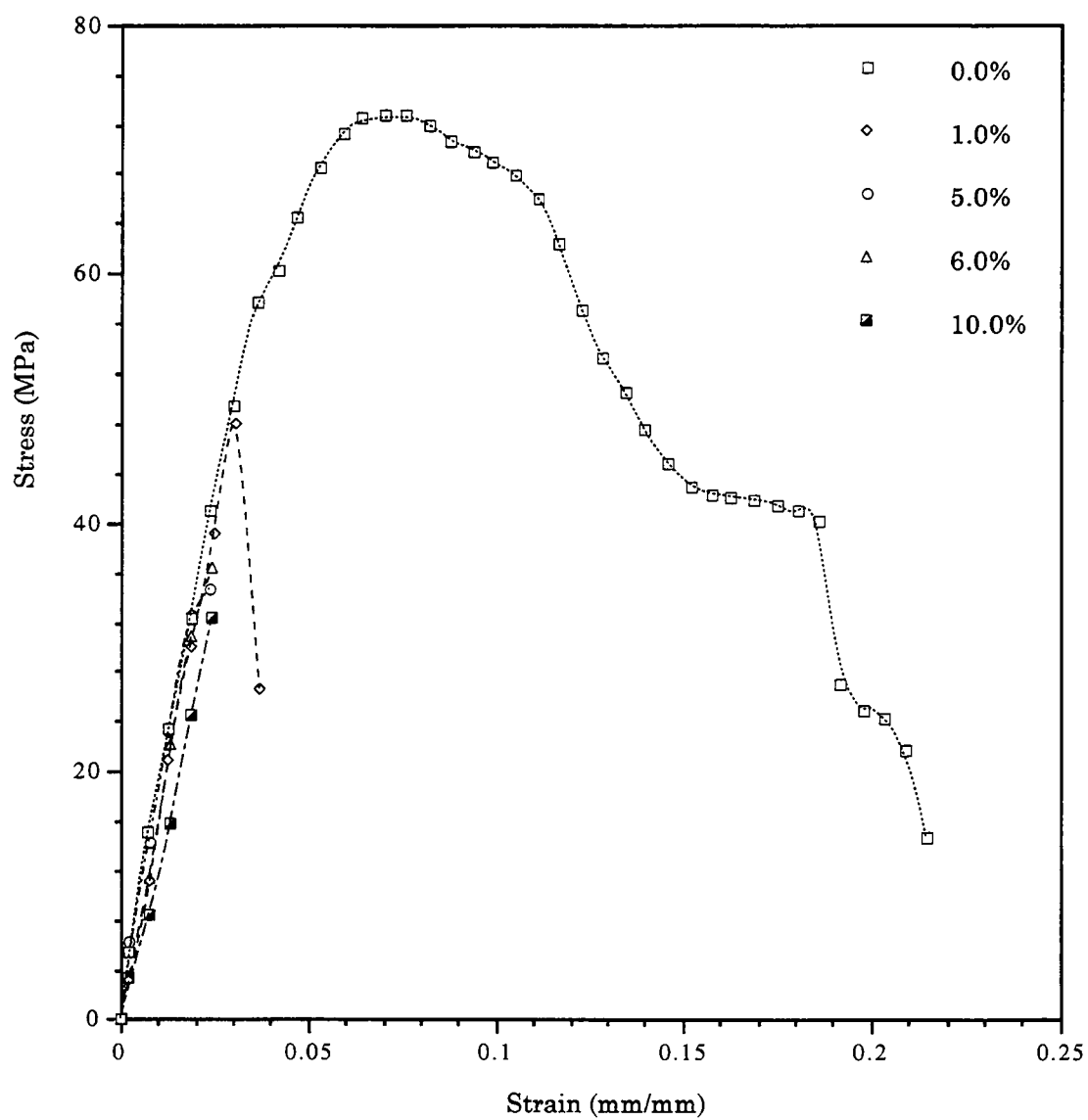


Figure 13. Representative tensile curves of dry hydroxyapatite blends.

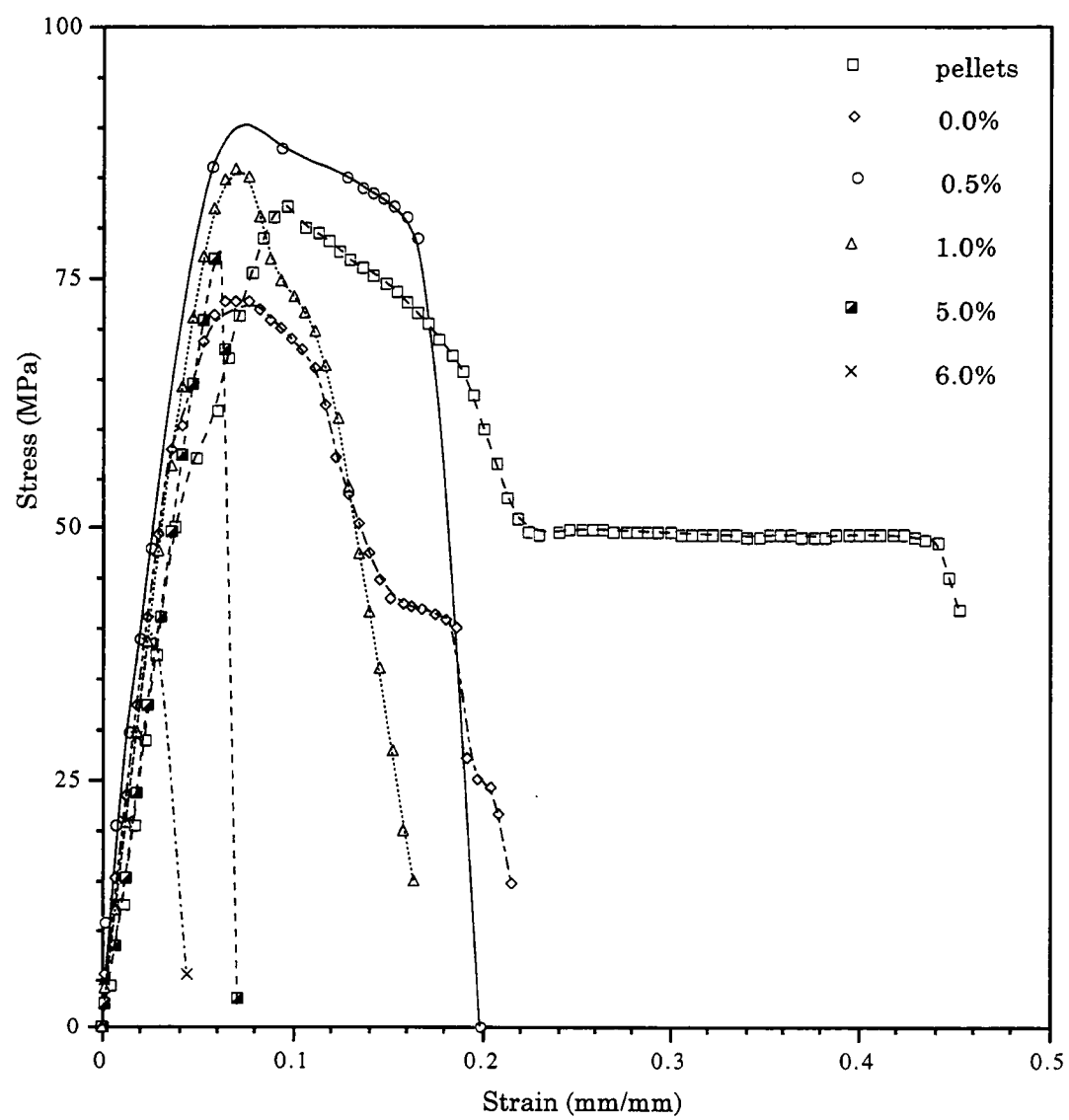


Figure 14. Representative tensile curves of dry CaCl_2 blends.

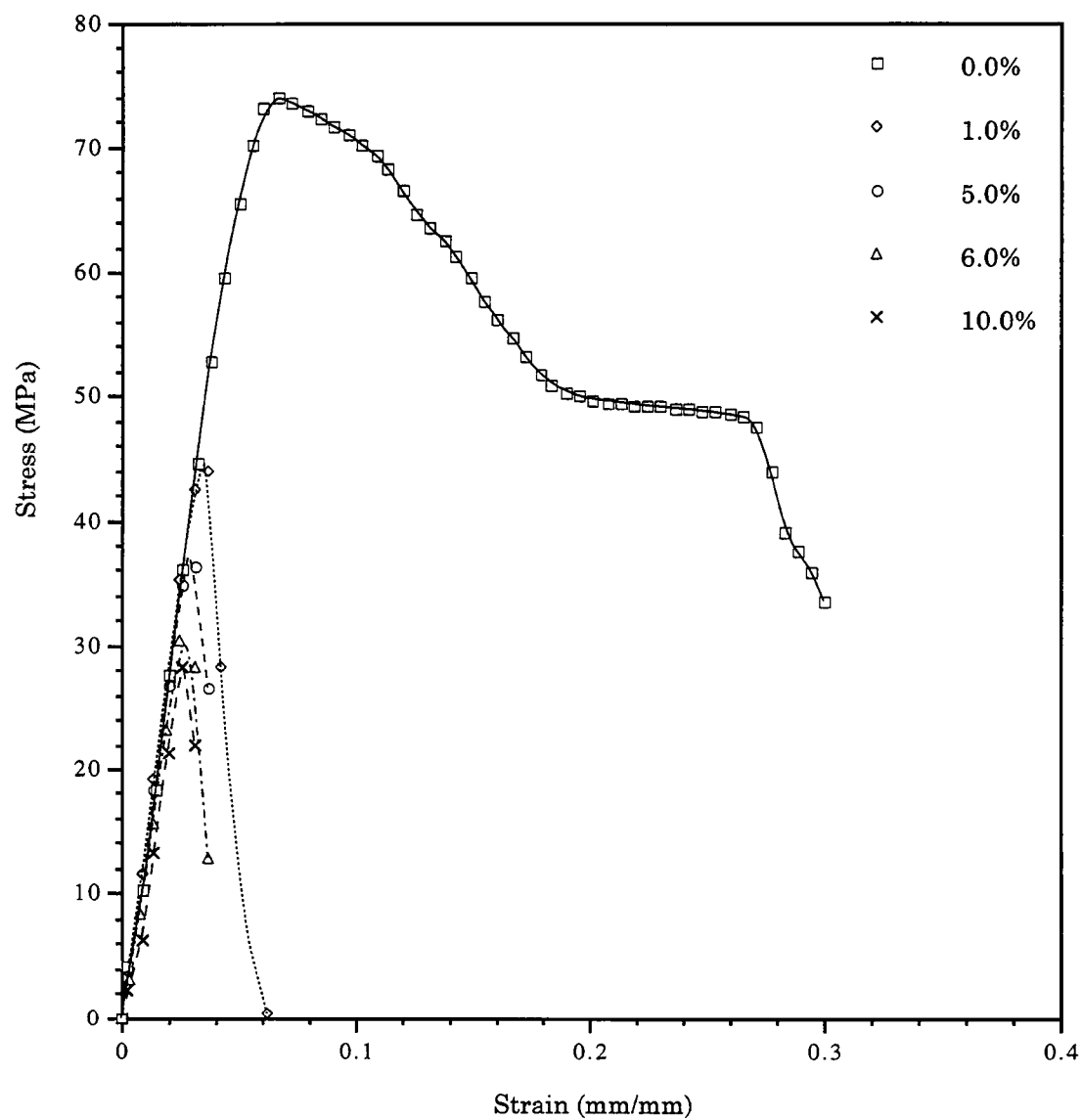


Figure 15. Representative curves for conditioned hydroxyapatite blends.

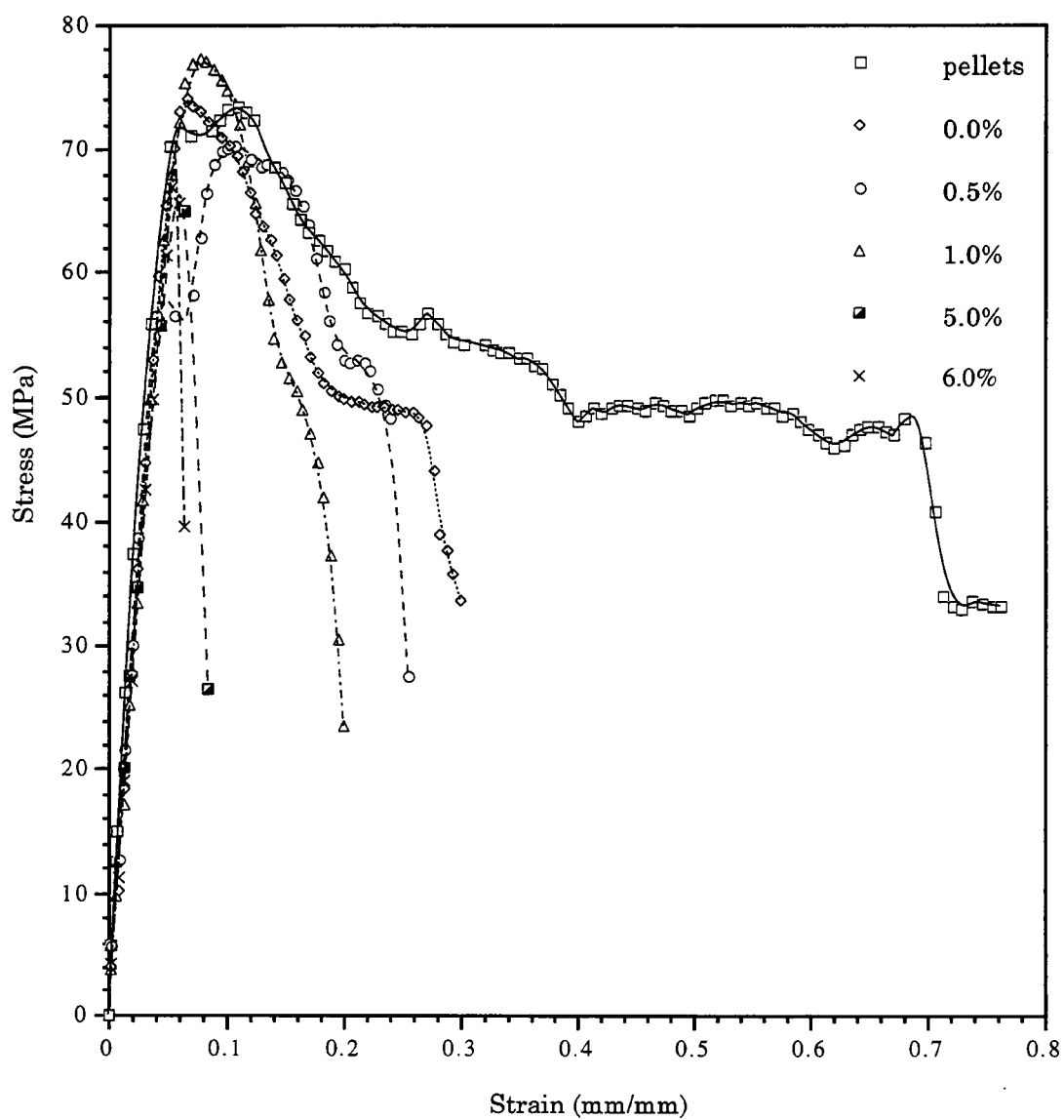


Figure 16. Representative tensile curves of conditioned CaCl_2 blends.

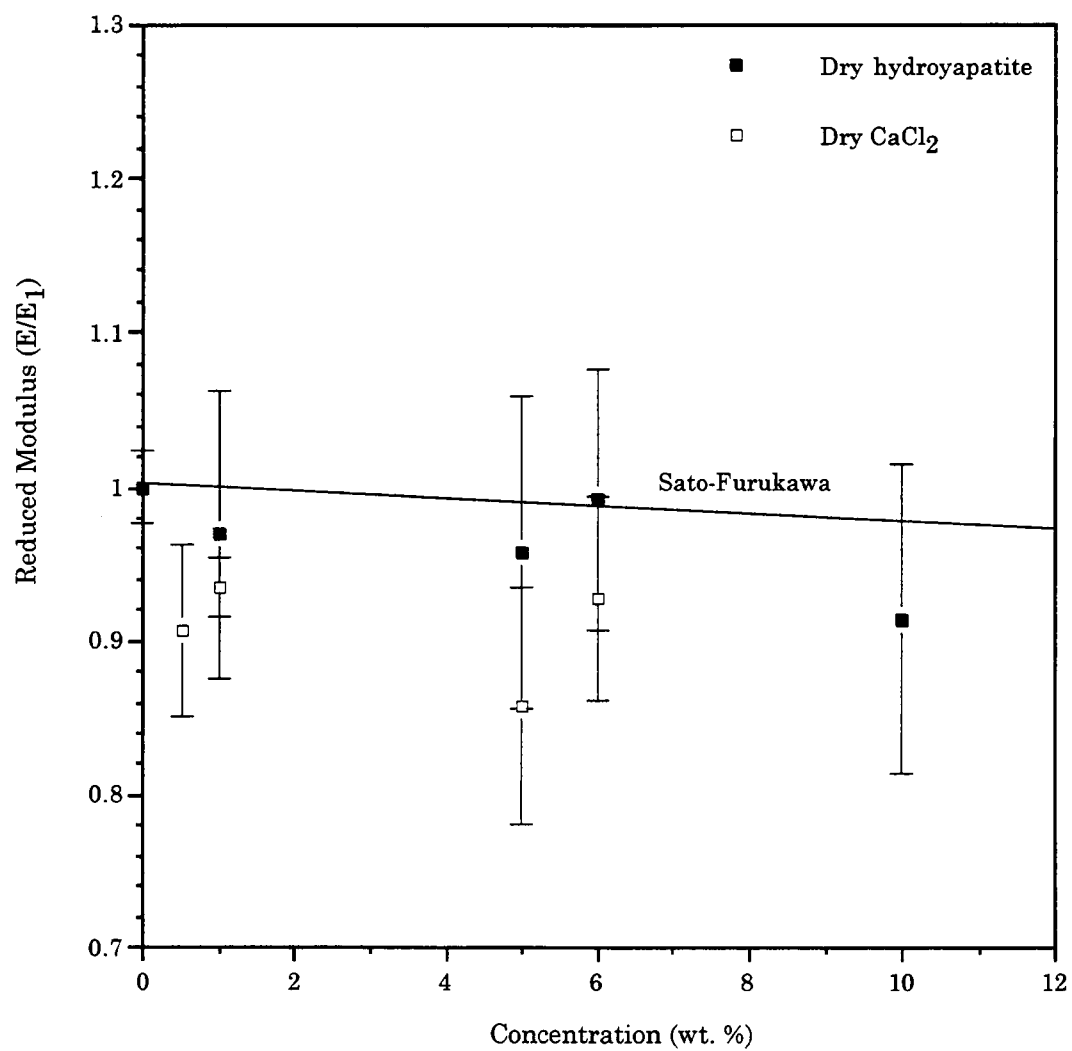


Figure 17. Reduced modulus of dry, molded samples.

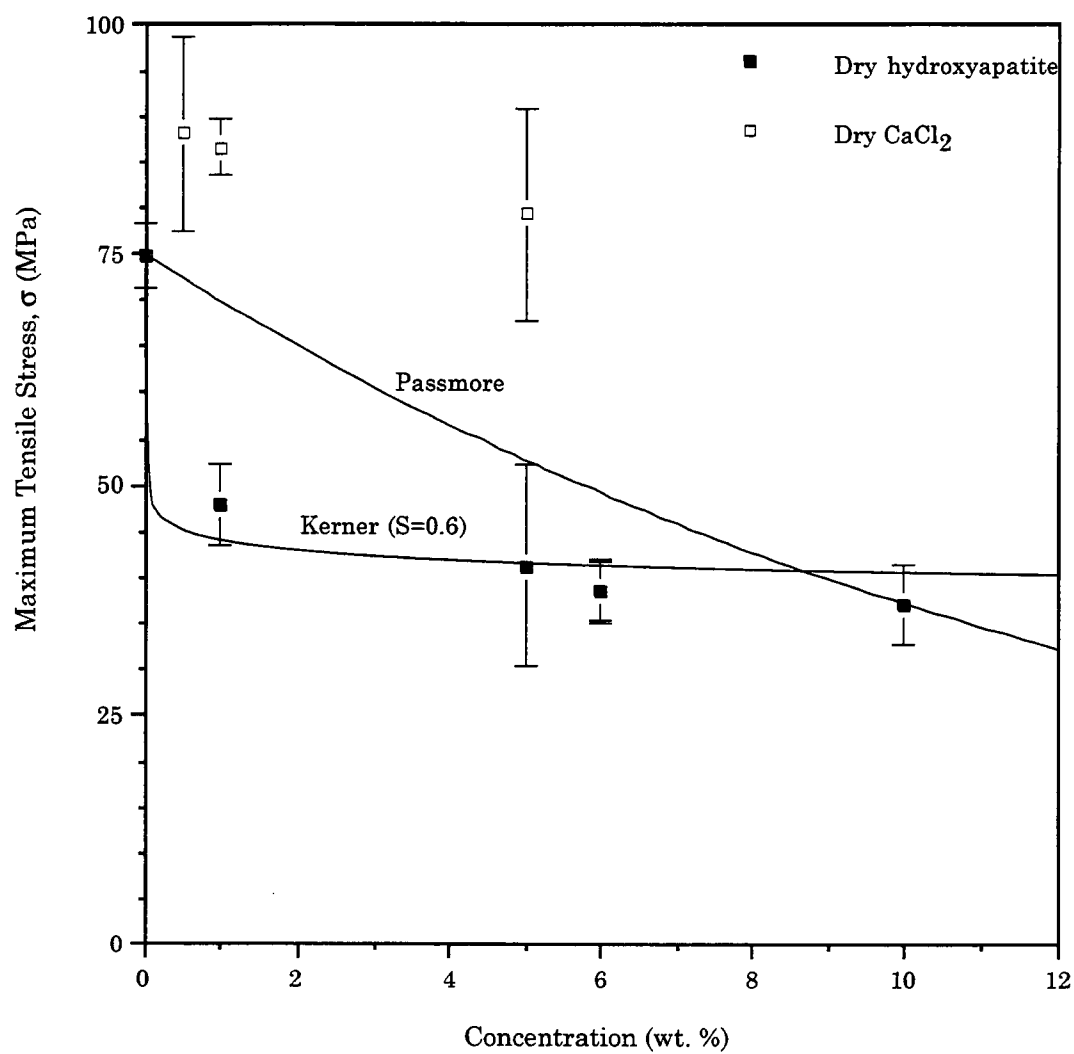


Figure 18. Tensile stresses of dry, molded samples.

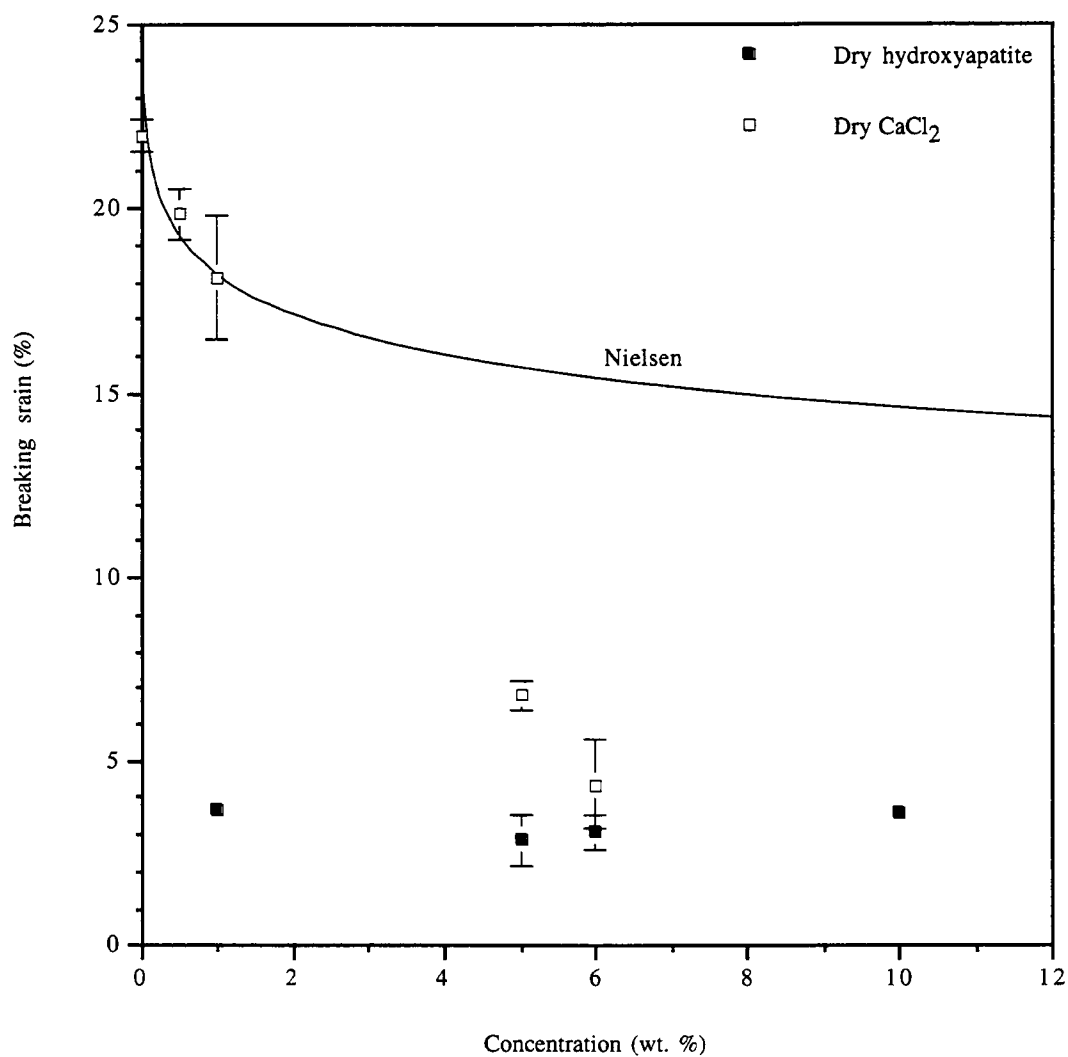


Figure 19. Breaking strain of dry, molded samples.

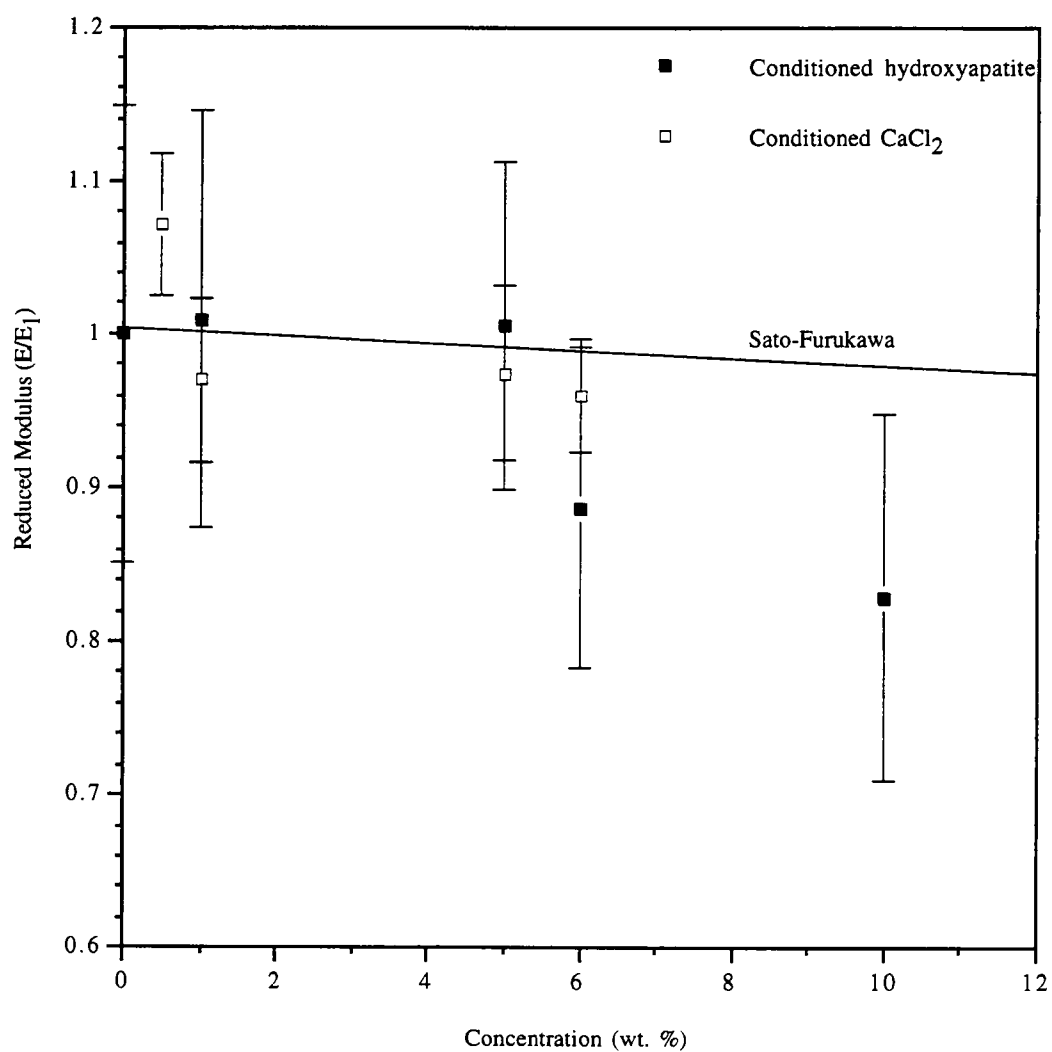


Figure 20. Reduced modulus of conditioned, molded samples.

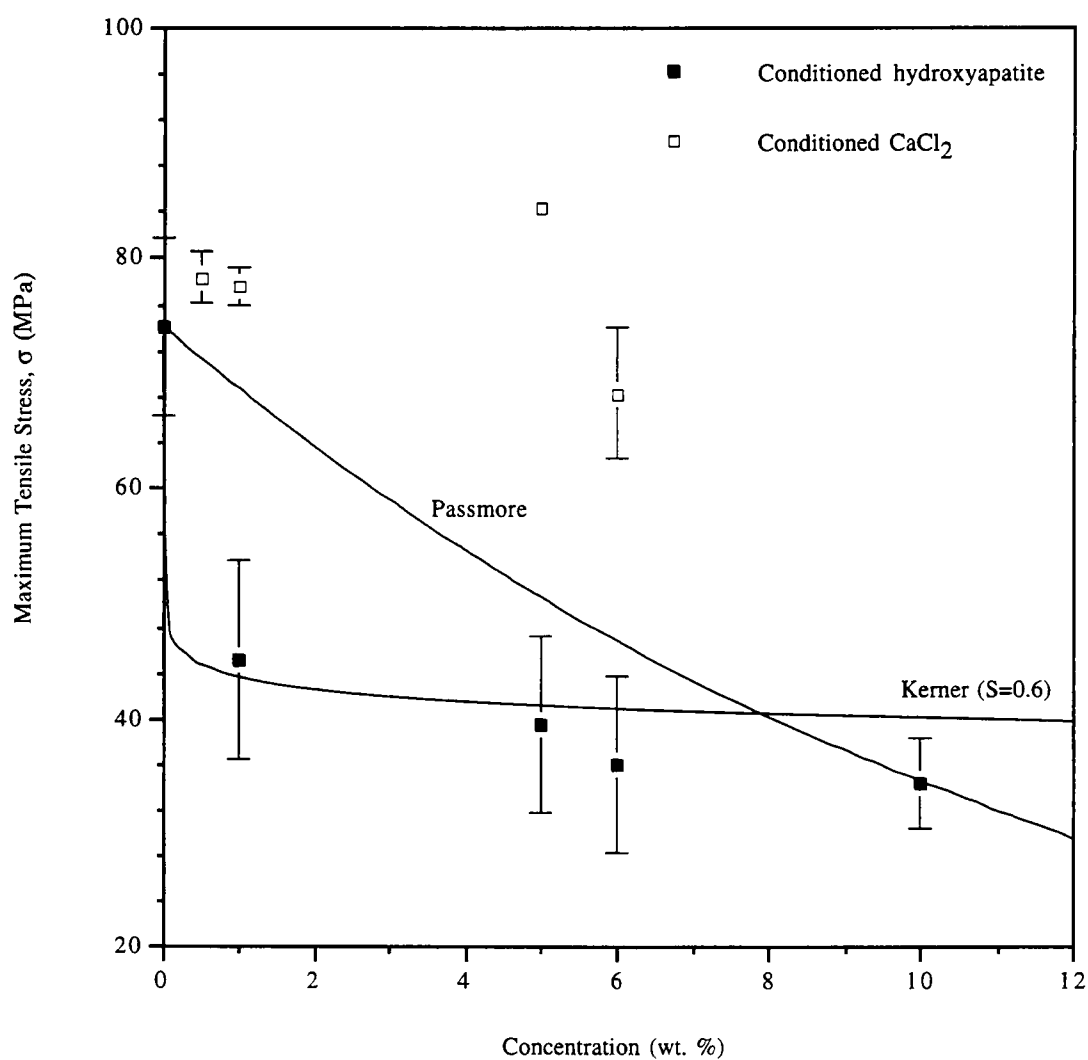


Figure 21. Tensile stresses of conditioned, molded samples.

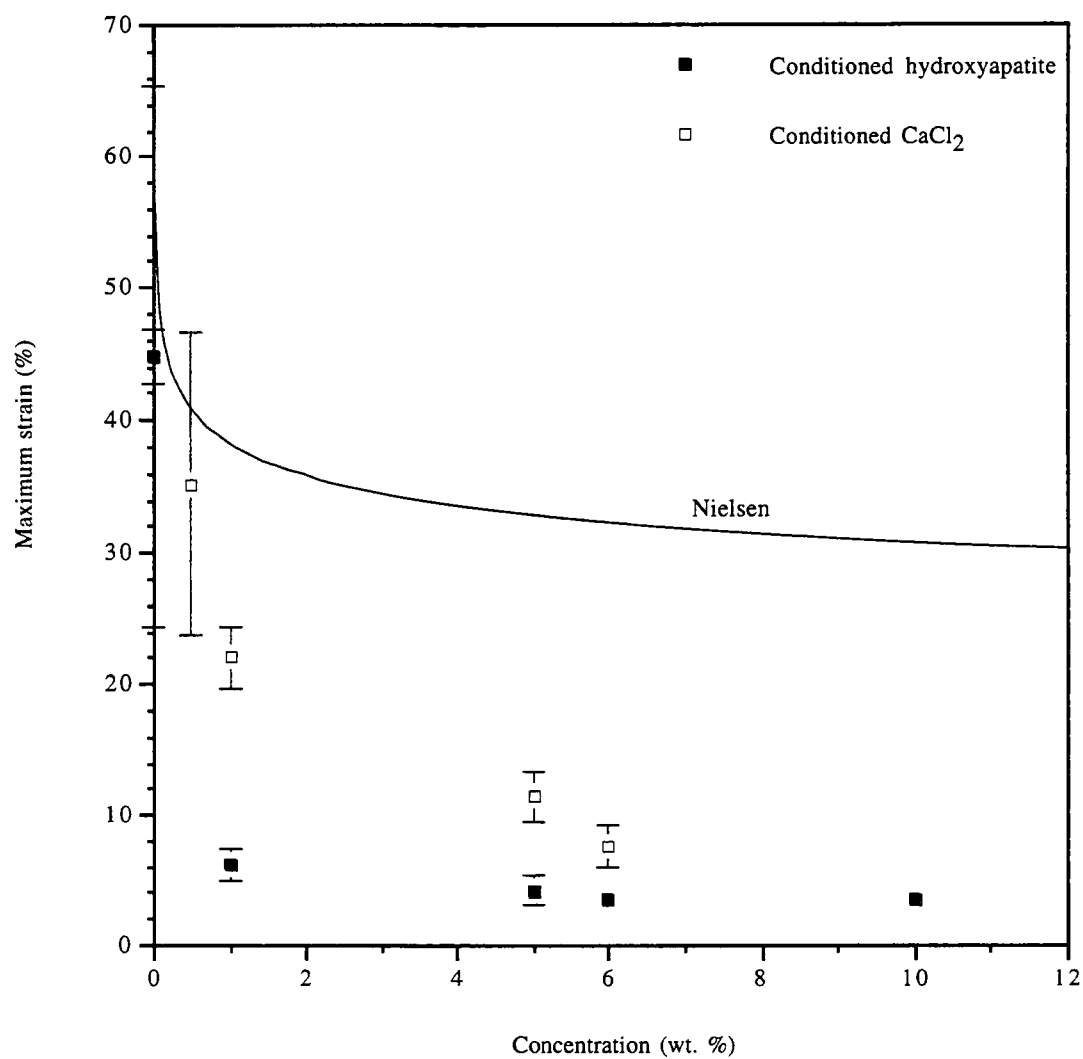


Figure 22. Breaking strain of conditioned, molded samples.

The pellets and solution cast samples exhibit similar properties in the conditioned state, but not so in the dry condition. The modulus is higher in the solution cast material, but this comes at the cost of a reduction in strain and tensile strength. The effect of moisture will be discussed in the next chapter.

The hydroxyapatite blends, dry and conditioned, both exhibited marked decreases in the Young's modulus, but more so in the wet samples. With increasing amounts of calcium phosphate salt, the modulus decreased accordingly. This same trend was also evident in the maximum tensile stress. This is illustrated by the fact that the 10.0% HA maximum tensile stress was more than 50% lower in magnitude than that for the 0.0% solution sample. This decrease would seem to indicate that the matrix is still the main load bearing phase. The ramifications of this will also be discussed in the next chapter.

All hydroxyapatite blends also exhibited an extreme loss in ductility. The strain to break compared to both solution and as-received pure materials is significantly lower. This could be due to the fact that hydroxyapatite is an insoluble salt and did not bond sufficiently with the matrix, causing voids.

Barring the initial drop in modulus compared to the 0.0% solution sample, the CaCl_2 blends did not change significantly. As the salt composition increased, the modulus did not change within the standard deviations of the samples. The conditioned samples of CaCl_2 as well, did not change significantly throughout the different composition changes.

Maximum tensile stresses for the dry CaCl_2 blends, however, changed significantly, especially in the lower concentrations of salt. In contrast to the hydroxyapatite blends the CaCl_2 salt affected the matrix such that the stress increased at small concentrations. This did not continue into the higher

concentrations, which exhibited an actual loss at the maximum concentration of 6.0% CaCl_2 .

Strain reductions also occurred in the CaCl_2 blends, although initially not to the same degree as the hydroxyapatite specimens. They do, however, exhibit a trend that approaches the same minimum as the hydroxyapatite. Clearly, the fact that CaCl_2 is a salt capable of disassociating has a distinct effect on its incorporation into the polyamide matrix.

The prediction used for calculating the reduced modulus is that proposed by Sato and Furukawa in which case the addition of filler actually decreases the reduced modulus, E/E_1 . For all concentrations, the weight percent of the filler has been converted to volume fraction for the indicated calculations. The densities required for this conversion are 1.15 g/cm^3 for pure nylon, which assumes the degree of crystallinity, χ_c , is 35% (will be discussed later) and 2.512 and 3.219 g/cm^3 for CaCl_2 and hydroxyapatite, respectively. The accuracy of the prediction appears to be greatest for that of the dry hydroxyapatite specimens. The most that can be said in the case for the CaCl_2 blends is that they follow the same trend of an overall decrease in the reduced modulus.

The Kerner prediction in which the filler content is modeled similar to that of void spaces shows good agreement to the hydroxyapatite blends. This is true for both the dry and conditioned examples. The Kerner equation tends to level off at higher concentrations, however, while the experimental values continue to decrease. With respect to the Passmore prediction, the exponential decay in regards to volume fraction of filler is hardly valid. It does not consider the sharp initial drop in stress with the inclusion of even small amounts of salt.

Noticeably absent in the tensile stress figures is a prediction for the behavior of the CaCl_2 blends. The mathematical models presented here appear to offer no viable prediction for the behavior observed. This is the case for both dry and conditioned samples of CaCl_2 . The initial increase and subsequent decrease in tensile stresses is not easily predicted by these simple filler models. The lack of a predictive model may be a result of the disassociation of the CaCl_2 ions. There exists, therefore, no "particulate" in the traditional sense to act as reinforcement. These considerations will be addressed further in the discussion.

Melt Pressed, Thin Samples

Physical property measurements for melt pressed samples of the salt blends differ in a few cases from those of the injection molded materials. The results of the thin plastic tensile tests are shown in Tables 7 and 8. Accompanying plots of reduced modulus and tensile stress versus concentration are presented in Figures 23-26. The breaking strain has been purposefully omitted from these figures due to the extreme variability in results. Some deviations exceeded the actual average values for a number of blends. An explanation for this variability will be addressed in the next chapter. The numerical values for the strains are still noted in the tables despite the error.

The dry hydroxyapatite samples exhibited similar behavior to that of the injection molded samples. The reduced modulus decreases with an increase in the salt concentration. The initial drop in modulus, however, is significantly lower than that of the injection molded samples. So much so that it is not represented by the Sato-Furukawa prediction. This is most likely due to the thin sample volume. Wet hydroxyapatite blends showed similar reduced modulus trends, except for the

Table 7. Tensile properties of dry, melt pressed blends.

Material	E (GPa)	$\sigma_{\max}$ (MPa)	Strain (%)
n6peldry - Dry as-received	1.79 ± 0.103	61.8 ± 1.37	179 ± 153
n6soldry - Dry from solution	1.77 ± 0.212	56.4 ± 9.17	151 ± 109
n605HAdry - 0.5% HA dry	1.25 ± 0.203	40.9 ± 2.84	88.5 ± 45.8
n601HAdry - 1.0% HA dry	1.23 ± 0.114	39.9 ± 5.68	37.4 ± 12.1
n650HAdry - 5.0% HA dry	1.39 ± 0.036	42.0 ± 0.49	19.6 ± 2.10
n660HAdry - 6.0% HA dry	1.20 ± 0.098	35.0 ± 3.23	16.8 ± 7.95
n610HAdry - 10.0% HA dry	1.25 ± 0.230	35.7 ± 6.86	12.5 ± 6.34
n605Cl dry - 0.5% CaCl ₂ dry	2.32 ± 0.223	67.2 ± 8.98	26.8 ± 12.7
n601Cl dry - 1.0% CaCl ₂ dry	2.37 ± 0.381	83.5 ± 18.8	61.2 ± 46.8
n650Cl dry - 5.0% CaCl ₂ dry	1.97 ± 0.161	85.3 ± 2.54	66.9 ± 61.4
n660Cl dry - 6.0% CaCl ₂ dry	1.50 ± 0.306	48.9 ± 9.79	38.2 ± 30.4

Table 8. Tensile properties of conditioned, melt pressed blends.

Material	E (GPa)	$\sigma_{\max}$ (MPa)	Strain (%)
n6pelwet - Wet as-received	0.576 ± 0.069	45.3 ± 13.4	172 ± 140
n6solwet - Wet from solution	0.931 ± 0.137	49.0 ± 5.05	192 ± 57.3
n605HAWet - 0.5% HA wet	0.784 ± 0.029	43.1 ± 7.48	92.5 ± 66.5
n601HAWet - 1.0% HA wet	0.817 ± 0.181	35.6 ± 5.66	13.1 ± 4.11
n650HAWet - 5.0% HA wet	0.826 ± 0.103	33.7 ± 4.92	11.7 ± 11.9
n660HAWet - 6.0% HA wet	0.917 ± 0.089	33.3 ± 2.10	15.4 ± 4.53
n610HAWet - 10.0% HA wet	1.16 ± 0.410	32.3 ± 8.94	5.05 ± 1.43
n605Clwet - 0.5% CaCl ₂ wet	0.734 ± 0.062	47.2 ± 11.0	44.0 ± 30.7
n601Clwet - 1.0% CaCl ₂ wet	0.760 ± 0.082	47.0 ± 1.57	60.7 ± 8.10
n650Clwet - 5.0% CaCl ₂ wet	1.48 ± 0.124	59.5 ± 9.46	266 ± 113
n660Clwet - 6.0% CaCl ₂ wet	1.61 ± 0.379	58.9 ± 12.0	30.9 ± 39.4

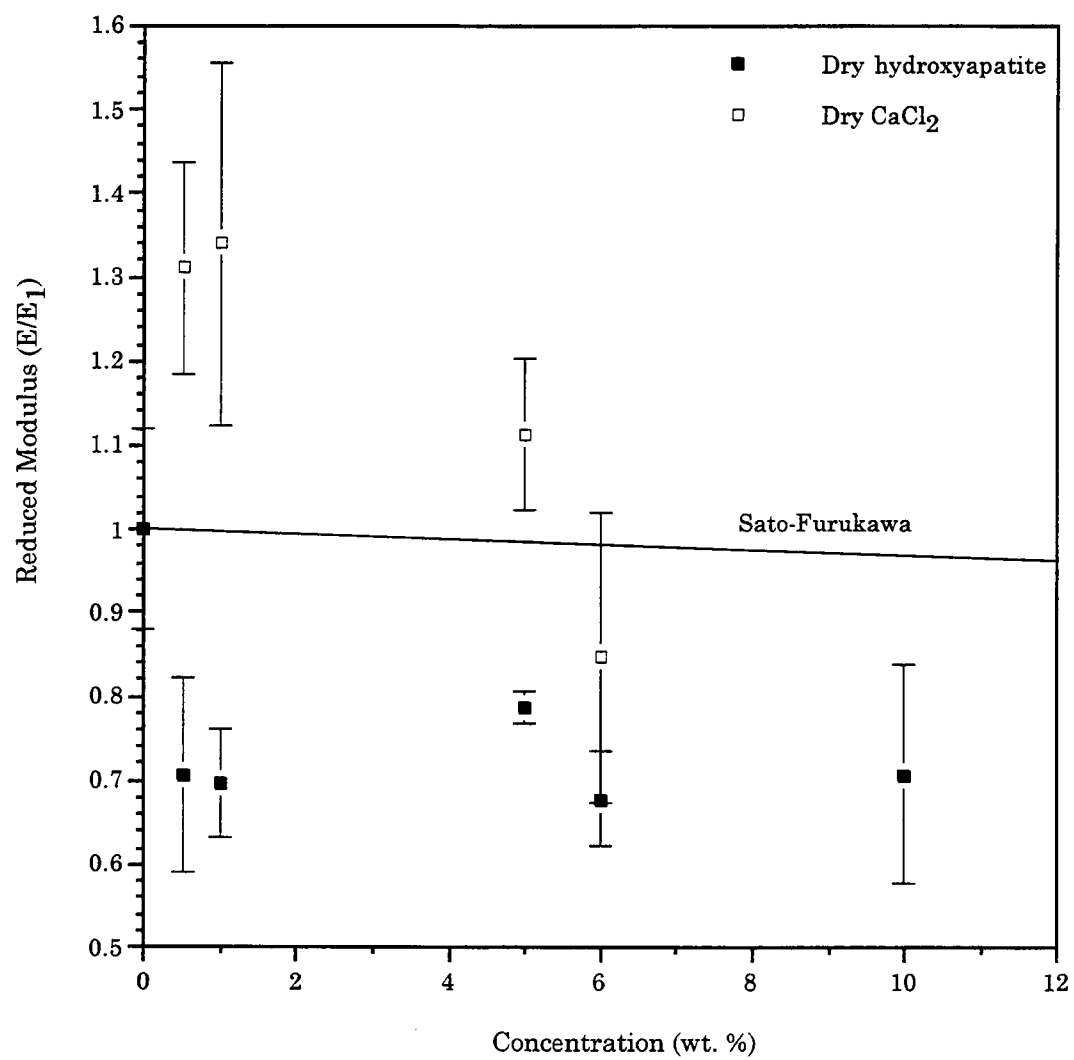


Figure 23. Reduced modulus for dry, melt pressed samples.

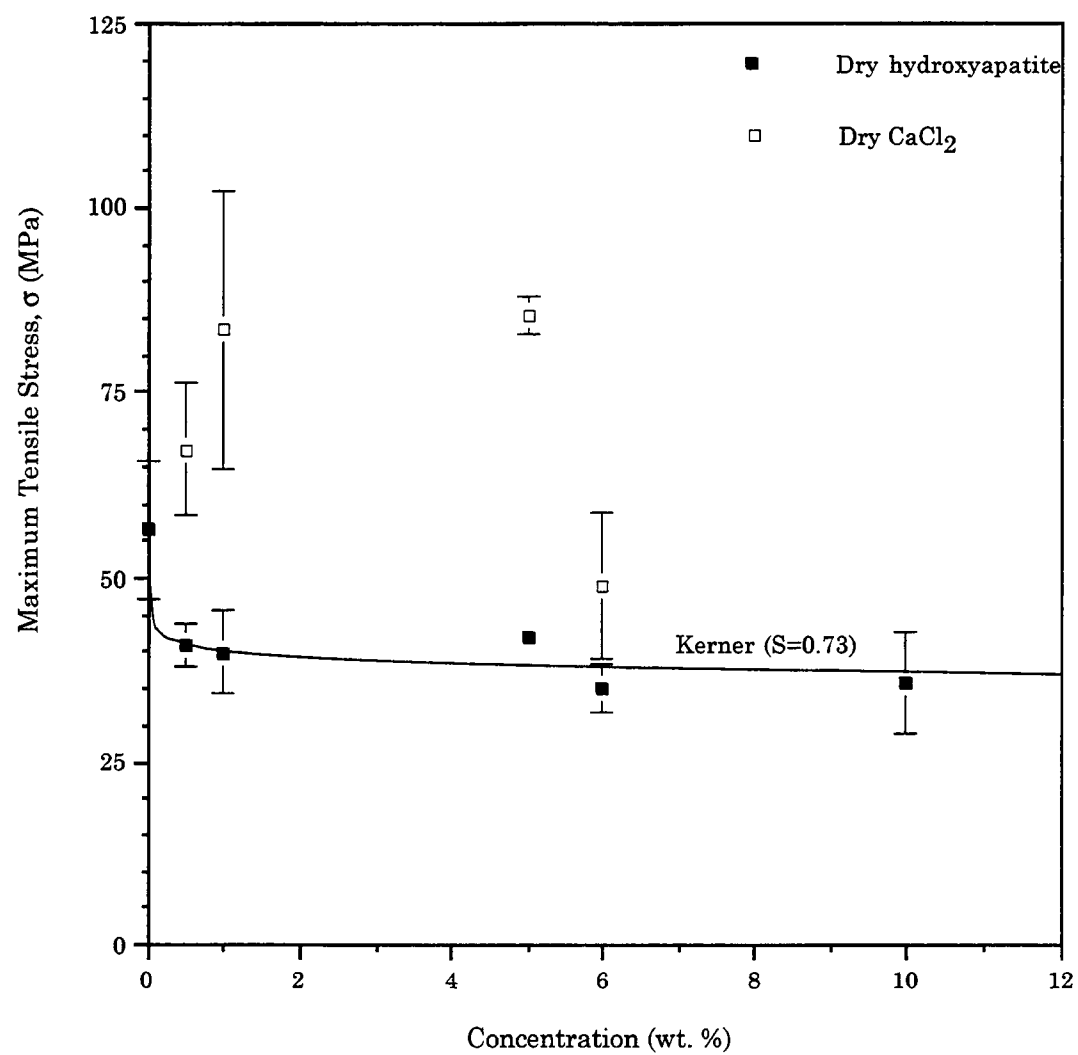


Figure 24. Tensile stresses of dry, melt pressed samples.

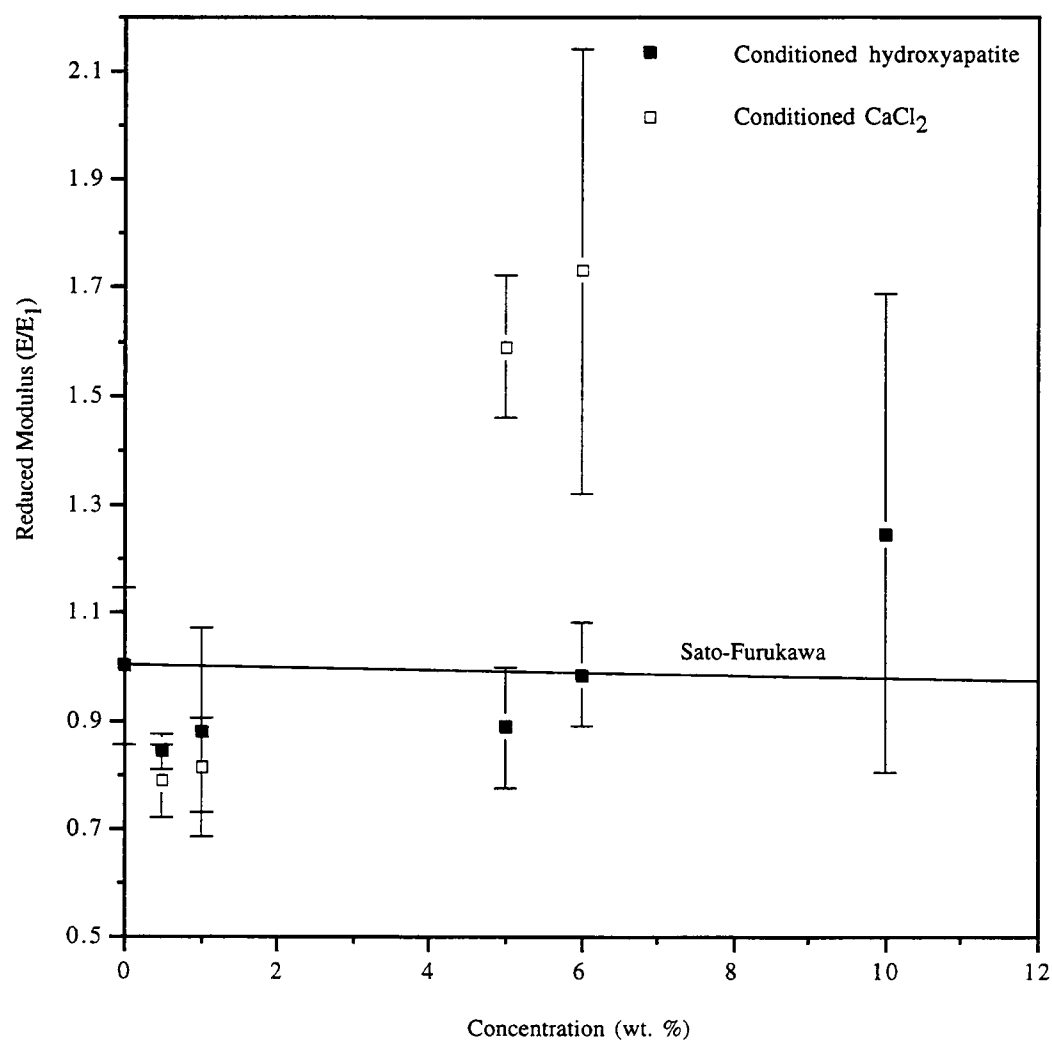


Figure 25. Reduced modulus of conditioned, melt pressed samples

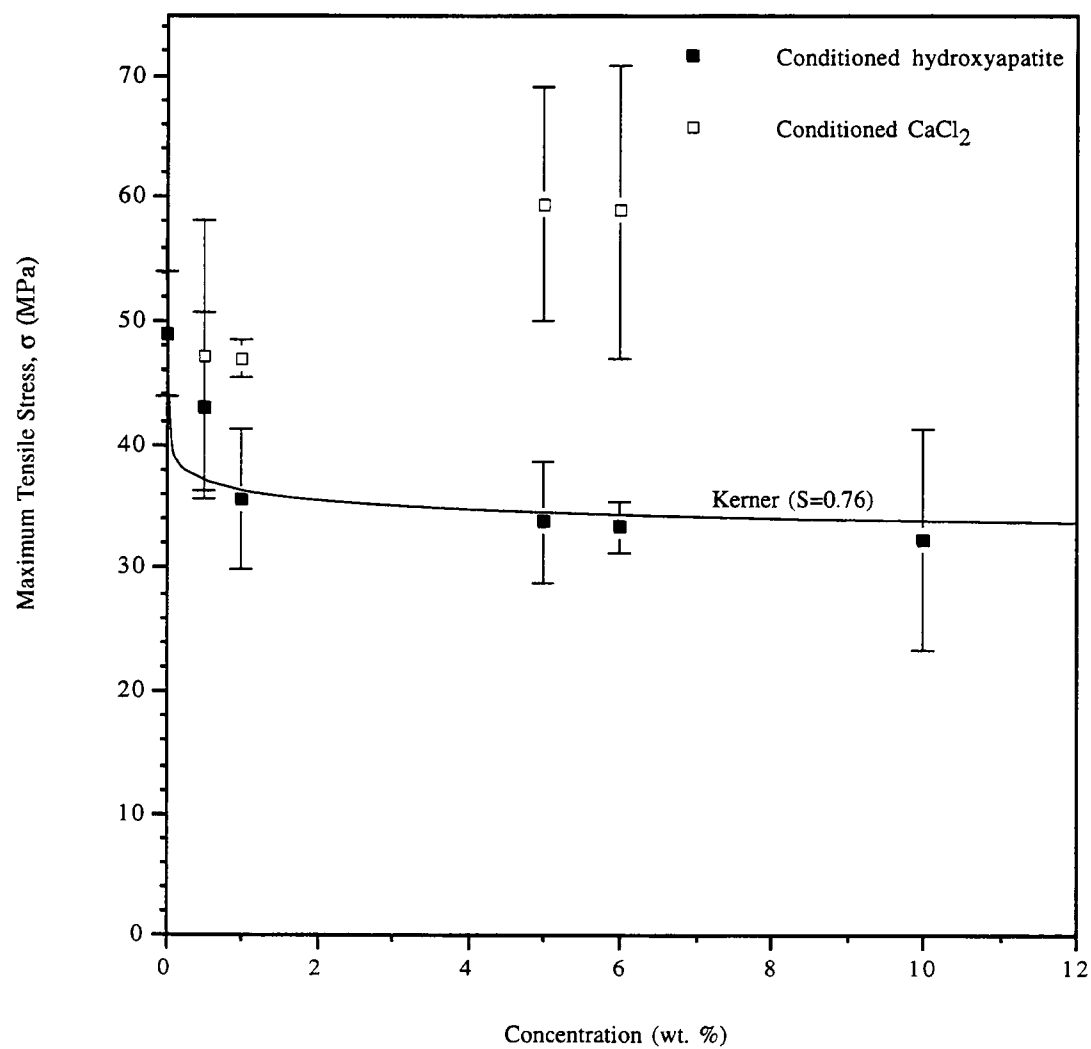


Figure 26. Tensile stresses of conditioned, melt pressed samples.

concentrations of 6.0% and 10.0% salt. These concentrations indicate an increase in modulus, contrary to that found for injection molded samples.

Tensile stresses in both dry and conditioned hydroxyapatite blends followed the same trend in reduction as those for injection molded samples. The Kerner theory appears also to be a valid prediction of the resulting properties. The curious anomaly, however, is that the concentration factor, S , that is used for the prediction is higher than that of the injection molded samples. There apparently is not as drastic an effect on the tensile properties for the thin film samples as with the injection molded materials.

Reduced modulus changes in the dry CaCl_2 blends also differ from those of its counterpart injection molded samples. The changes in this case are denoted by the rapid increase in modulus through 1.0% CaCl_2 . This is followed by a decrease to the point at which the resulting reduced modulus is lower than that predicted by the Sato-Furukawa method. The exact opposite, however, is found for the case of the conditioned blends. The elastic modulus in this case is at its maximum at a maximum concentration of salt.

The maximum tensile stresses of the dry CaCl_2 blends matched accordingly to the molded specimens. At low concentrations the tensile stress increased approximately 20-45%. The reinforcement then fell off after 5.0% CaCl_2 to a value below that of the pure material. Conditioned samples also displayed an increase in maximum tensile stress, but only at higher concentrations of salt. This shift in reinforcement may be due to the incorporation of water as a plasticizer as will be discussed in the next chapter.

Differential Scanning Calorimetry

Solution-cast Samples

The melting and crystallization characteristics of the solution cast blends are shown in Table 9. These results are the values determined from the peaks with the normalized thermal history (see Chapter II - Experimental). The reported peak position is that for the highest melting temperature as more than one melting peak was observed for a number of samples. Representative endothermic and exothermic plots for each of these blends are shown in Figures 27-41.

From the melting and crystallization data it is clear that subjecting the polymer pellets to the solution changes their crystallization behavior dramatically. The initial melting temperature of 236°C is reduced to 224°, a decrease of 12°C. Alternatively, the crystallization temperature increases by 9°C from 176°C to 185°C.

All hydroxyapatite blends displayed relatively no change in peak temperatures. These blends all have melting and crystallization temperatures that are within experimental error. It is clear as well, that little, or no change in the overall crystallinity takes place with higher incorporation of the phosphate salt. This phenomena is illustrated by the small changes in the melting peak area.

The addition of CaCl_2 to the polyamide resulted in large changes in melting temperature as well as crystallization. The melting temperature is seen to decrease in the matter of that predicted by Flory's calculations for interaction parameters. This correlation is illustrated in Figure 42 along with data for the crystallization temperature changes. Noticeably absent are peak temperatures for the 5.0% and 6.0% crystallization peaks as well as the melting peak for 6.0% CaCl_2 . Clearly the interactions of the salt were strong enough to depress the crystallization below the

Table 9. Average DSC thermal characteristics for all samples.

Material	T _m (°C)	ΔH _m (J/g)	T _c (°C)	ΔH _c (J/g)
As-received pellets	236	34	176	55
Solution - no salt	224	43	185	54
Precipitated polymer	225	54	184	62
0.5% HA	224	43	186	57
1.0% HA	225	45	185	55
5.0% HA	223	44	184	53
6.0% HA	224	43	185	55
10.0% HA	224	41	184	50
0.5% CaCl ₂	222	41	184	54
1.0% CaCl ₂	222	39	181	50
2.0% CaCl ₂	220	41	170	39
3.0% CaCl ₂	217	28	164	41
4.0% CaCl ₂	217	40	159	48
5.0% CaCl ₂	210	26	not observed	not observed
6.0% CaCl ₂	not observed	not observed	not observed	not observed

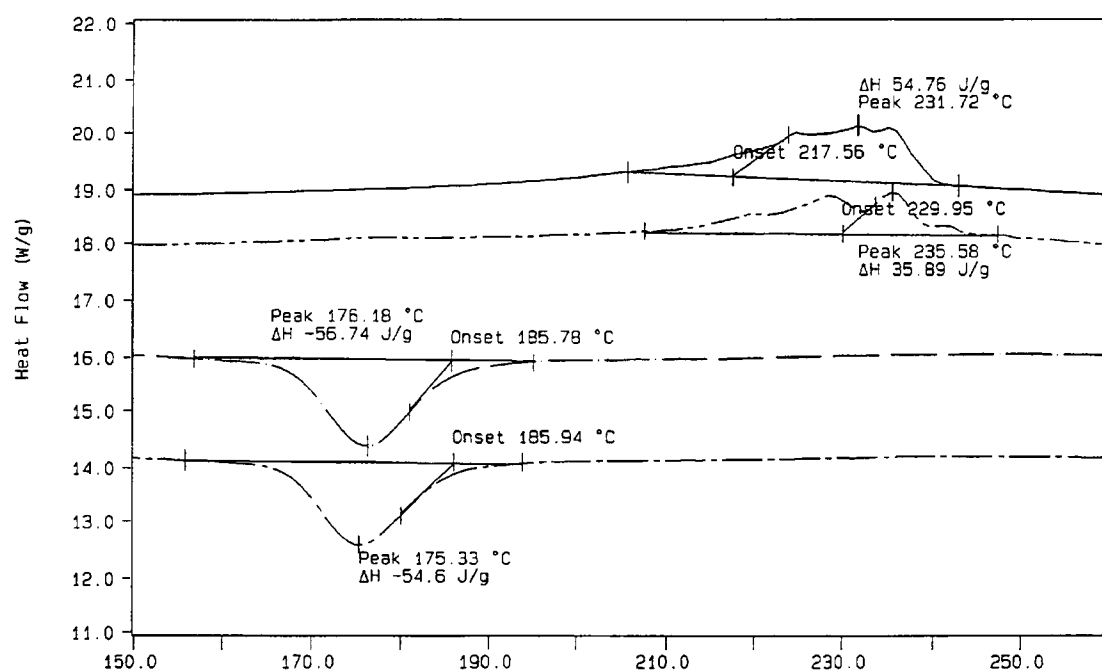


Figure 27. DSC thermogram of as-received pellets.

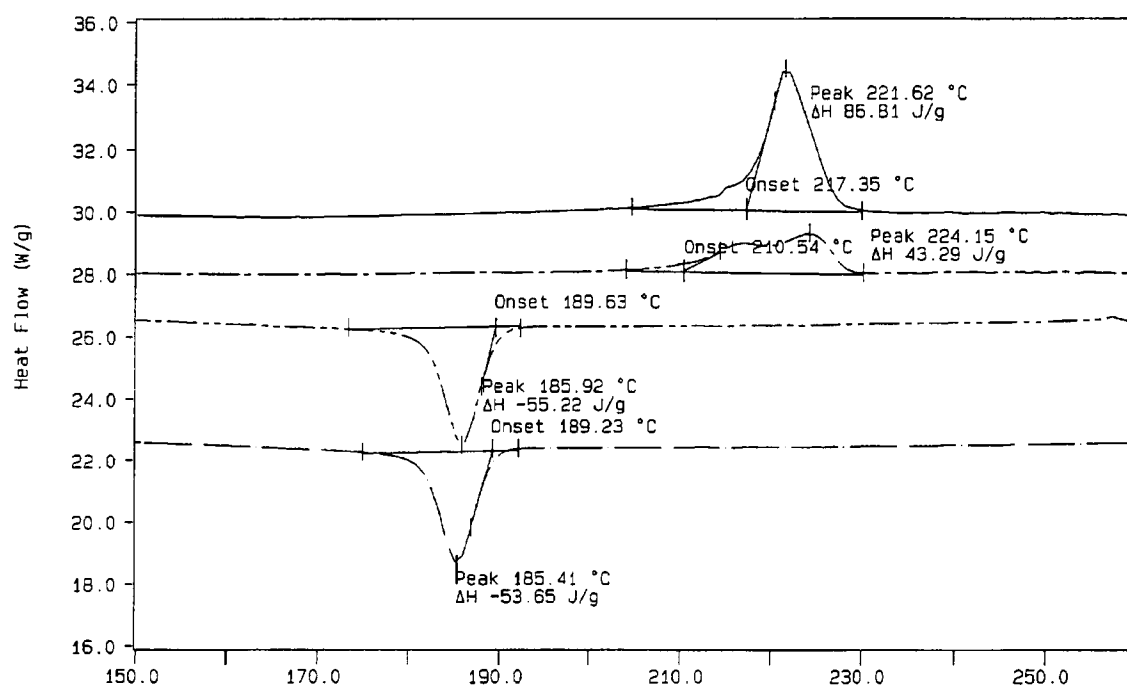


Figure 28. DSC thermogram of polyamide from solution.

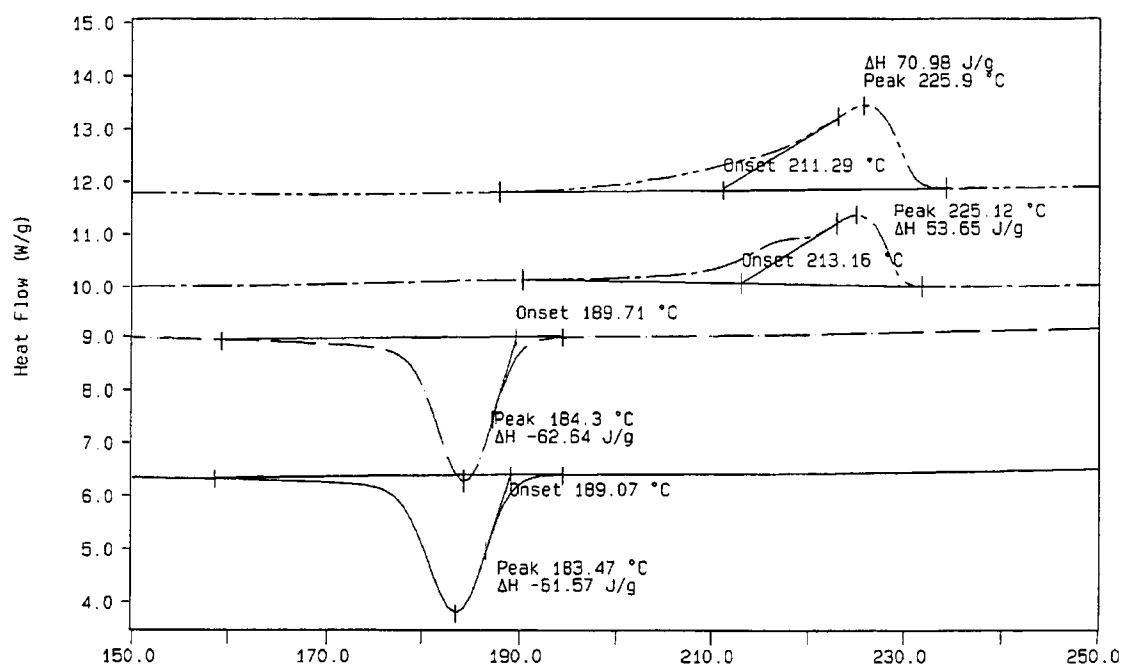


Figure 29. DSC thermogram of acetone-precipitated polyamide.

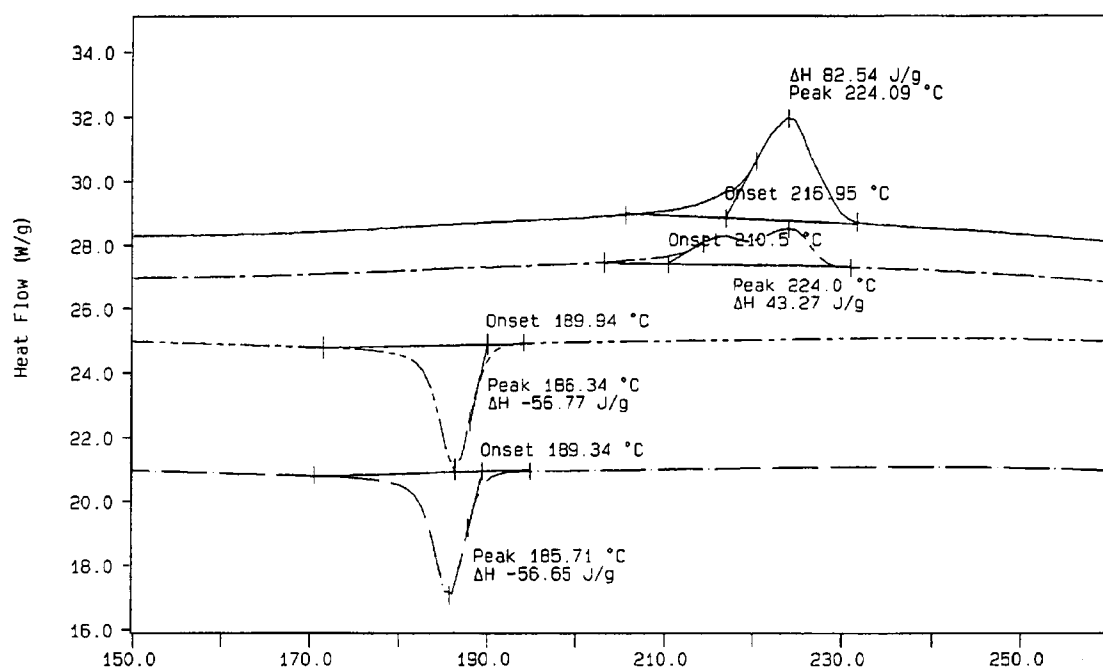


Figure 30. DSC thermogram of 0.5% hydroxyapatite blend.

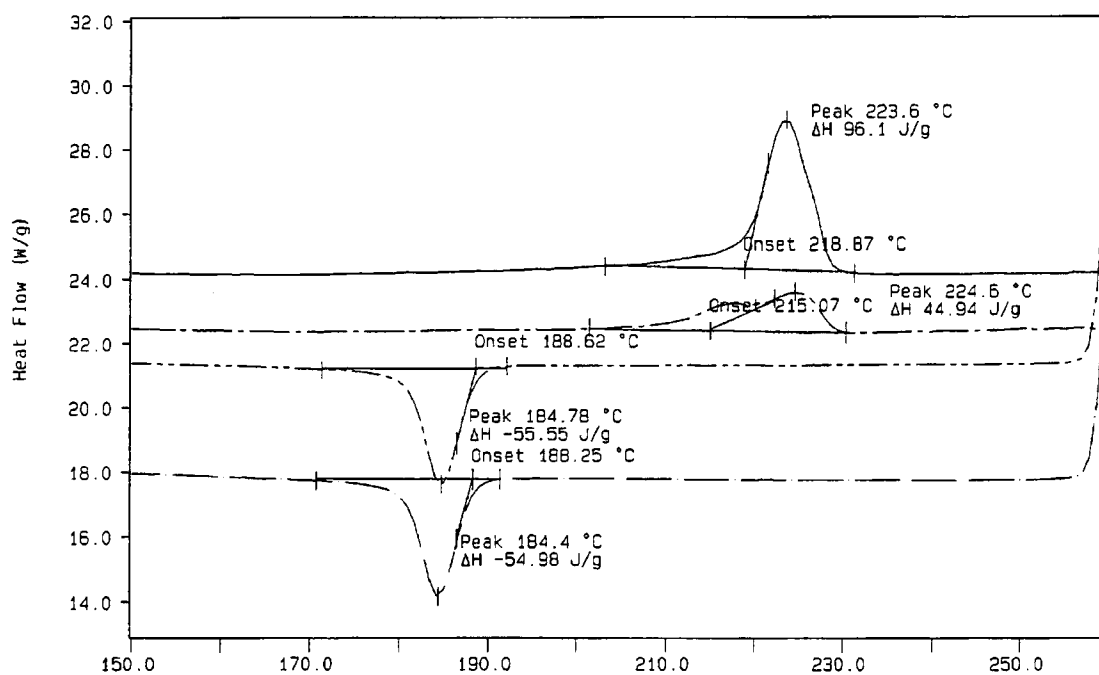


Figure 31. DSC thermogram of 1.0% hydroxyapatite blend.

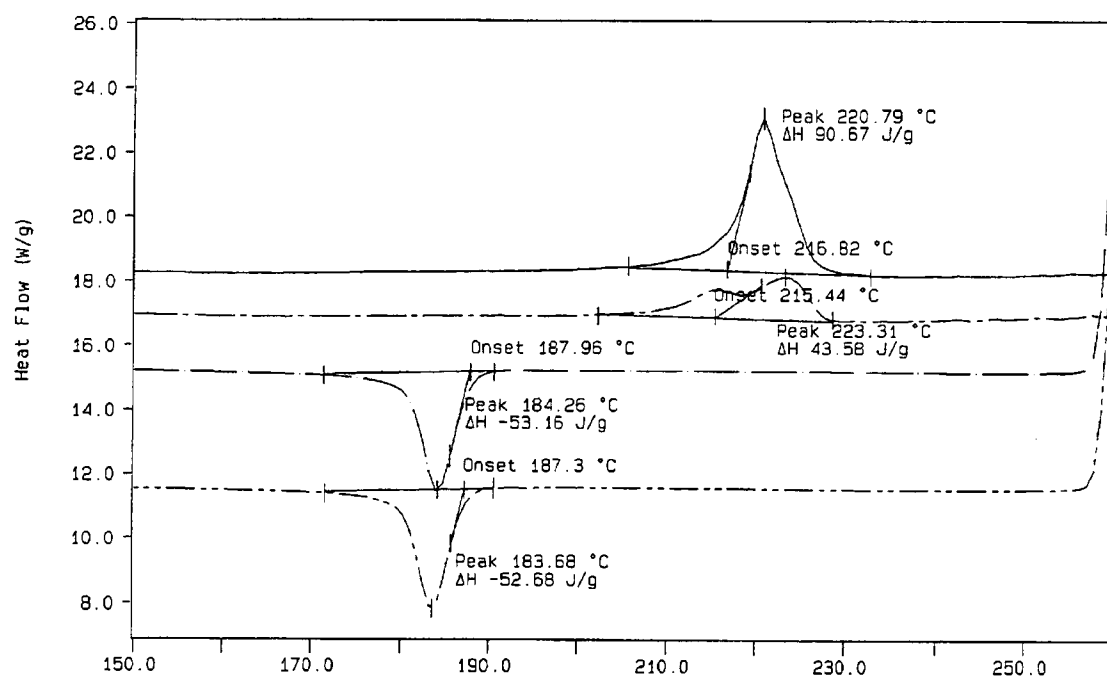


Figure 32. DSC thermogram of 5.0% hydroxyapatite blend.

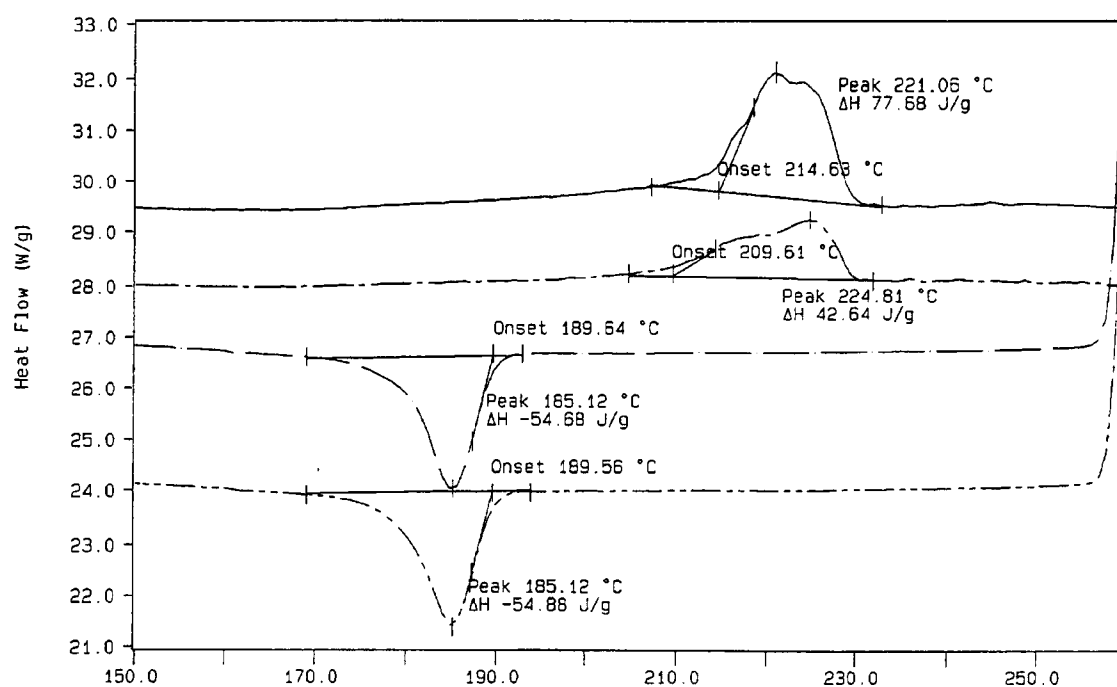


Figure 33. DSC thermogram of 6.0% hydroxyapatite blend.

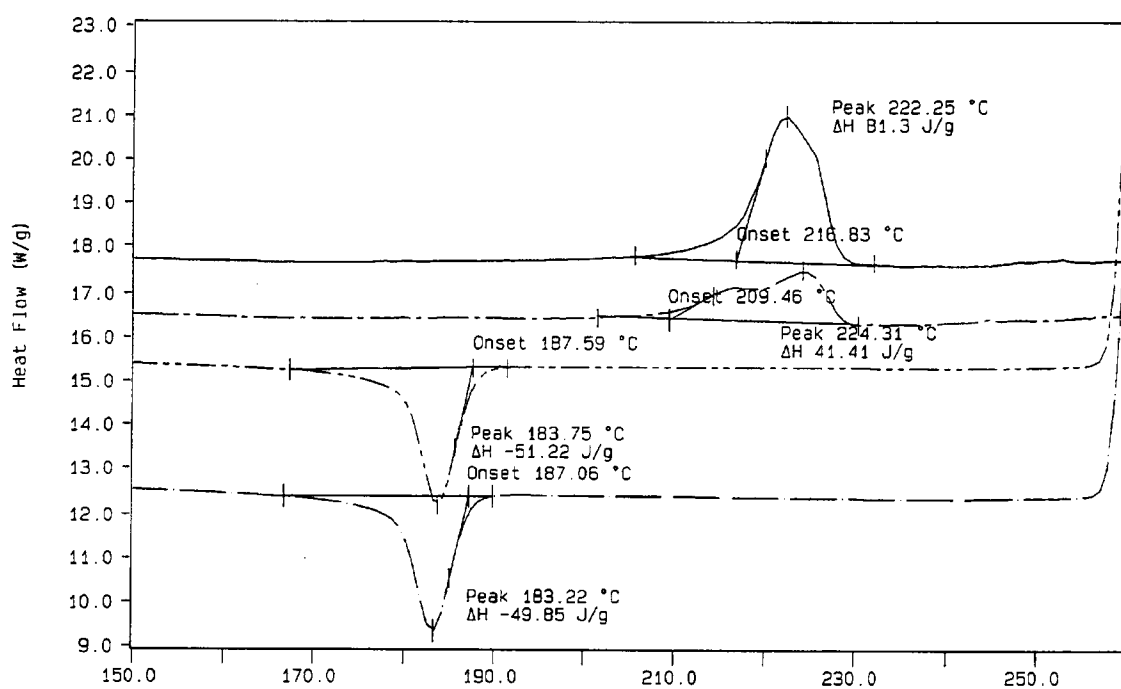


Figure 34. DSC thermogram of 10.0% hydroxyapatite blend.

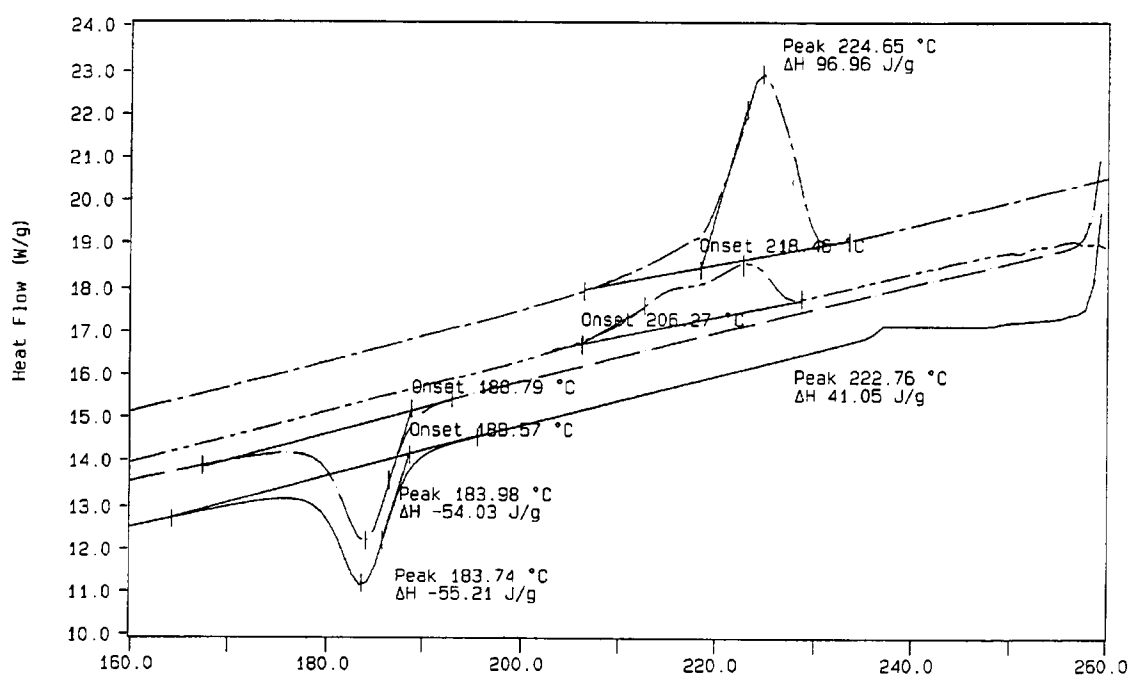


Figure 35. DSC thermogram of 0.5% CaCl_2 blend.

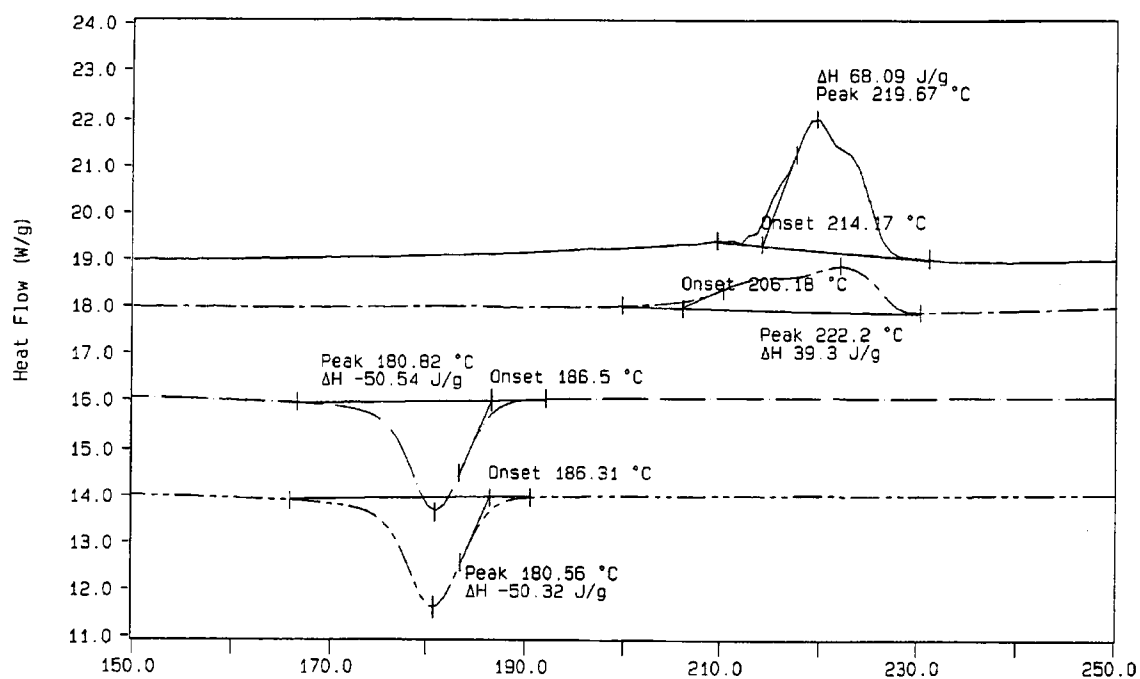


Figure 36. DSC thermogram of 1.0% CaCl_2 blend.

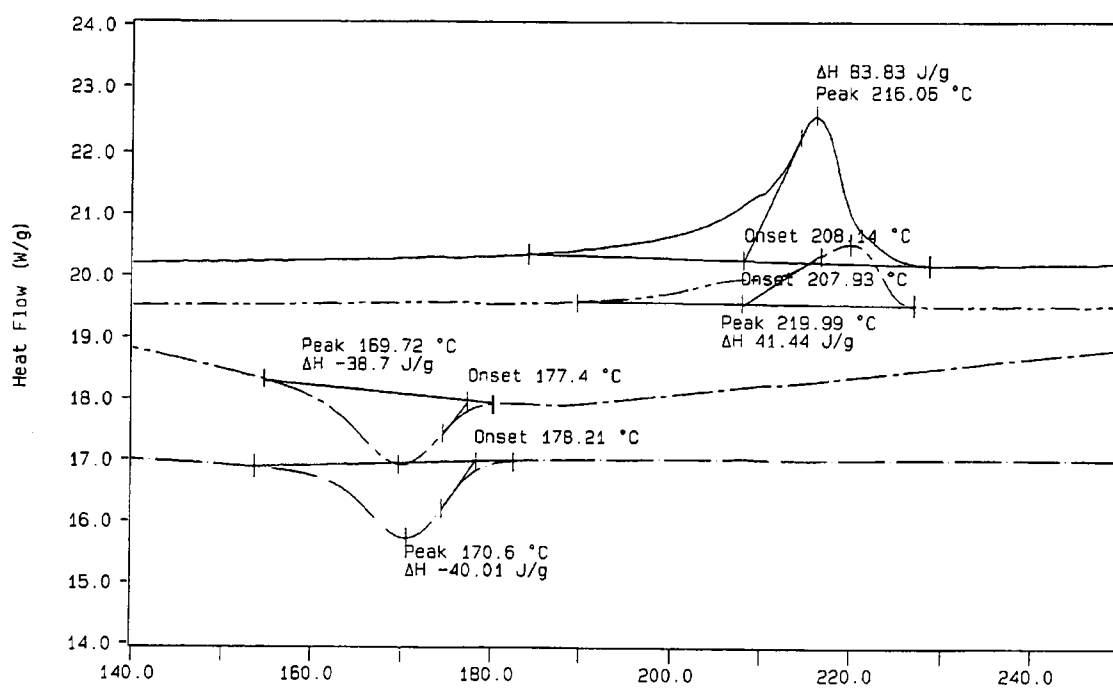


Figure 37. DSC thermogram of 2.0% CaCl_2 blend.

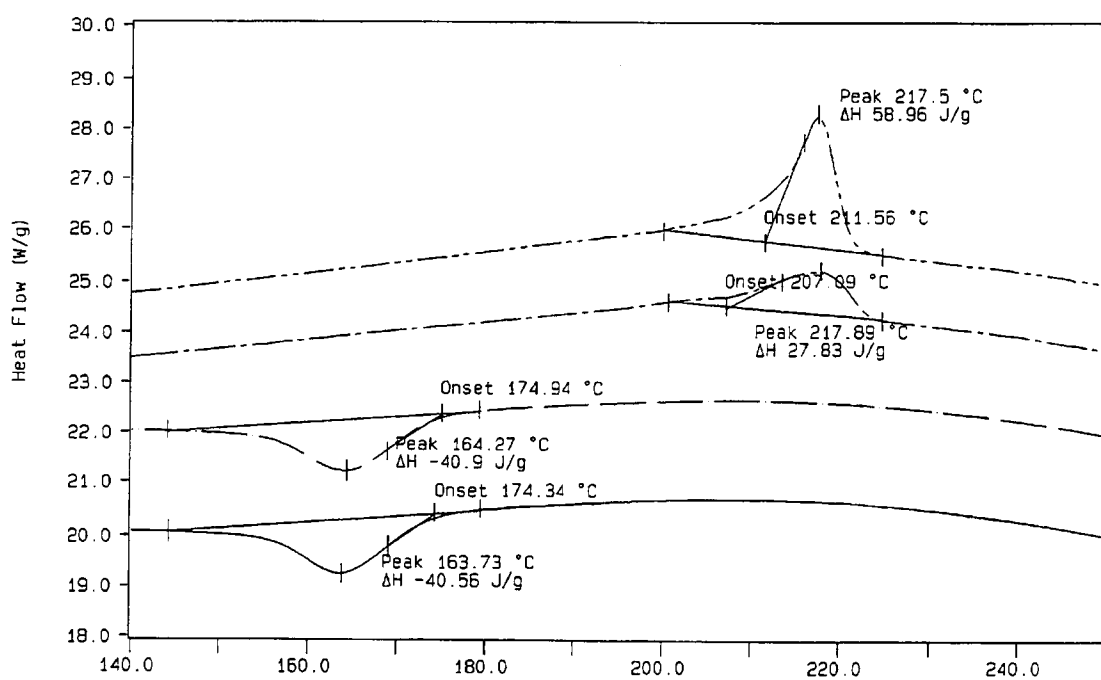


Figure 38. DSC thermogram of 3.0% CaCl_2 blend.

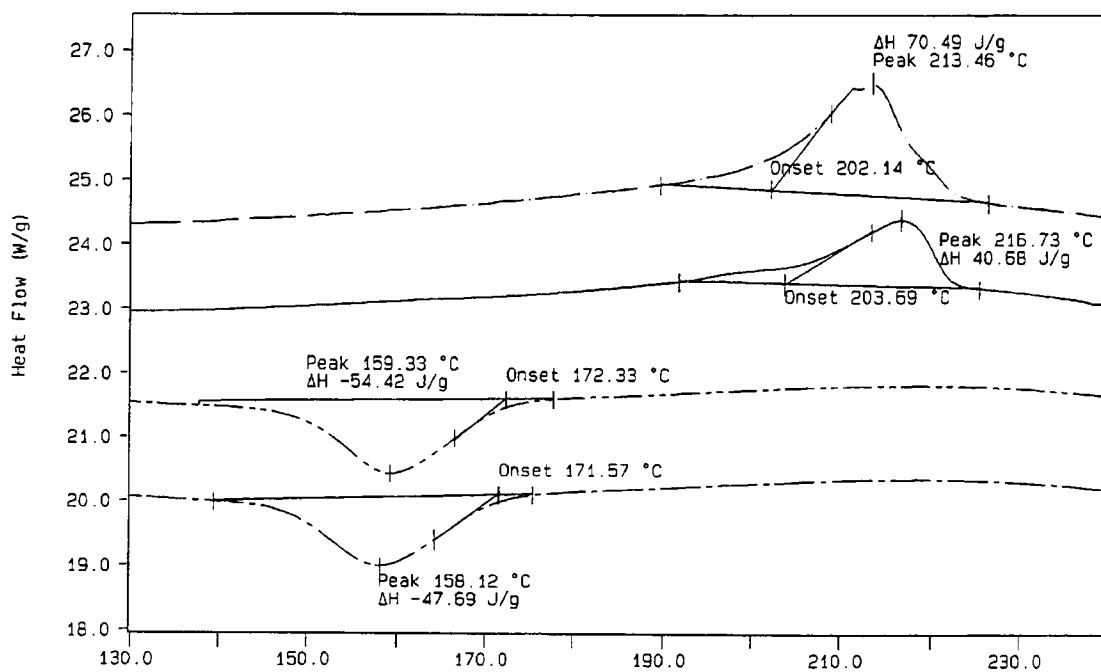


Figure 39. DSC thermogram of 4.0% CaCl_2 blend.

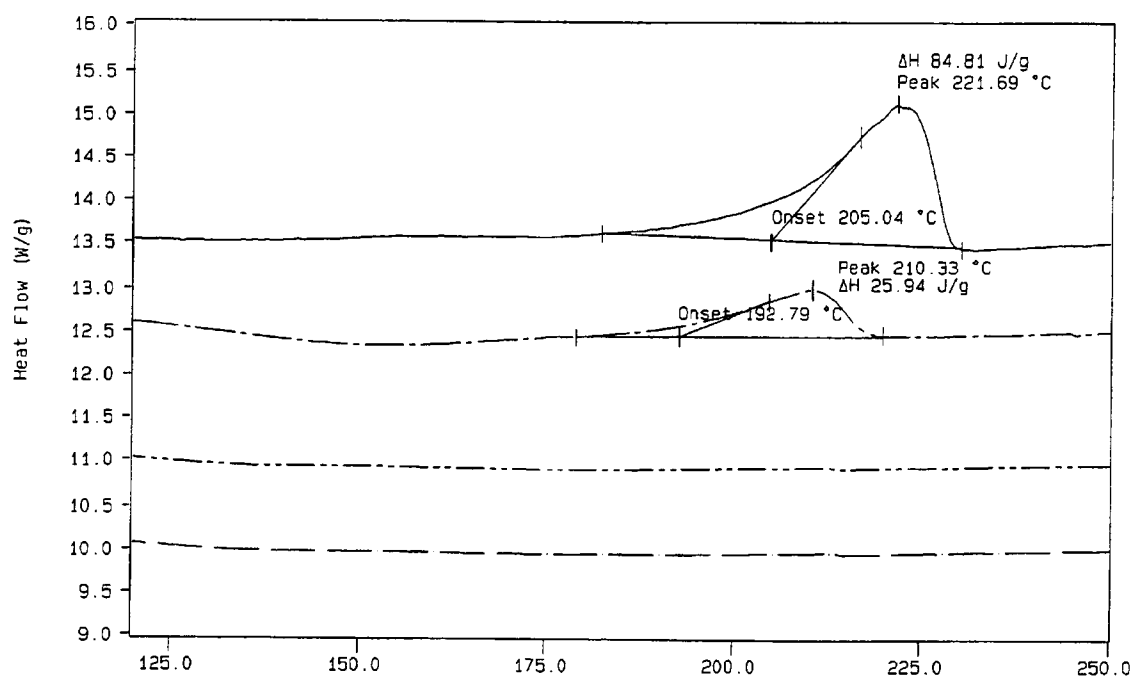


Figure 40. DSC thermogram of 5.0% CaCl_2 blend.

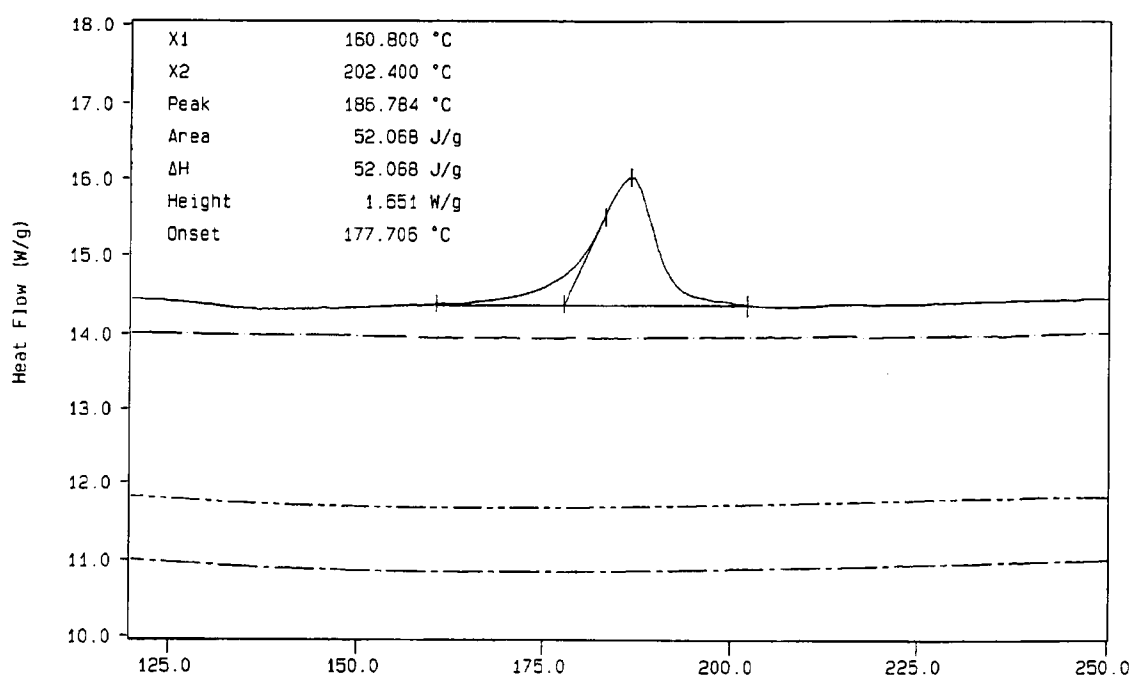


Figure 41. DSC thermogram of 6.0% CaCl_2 blend.

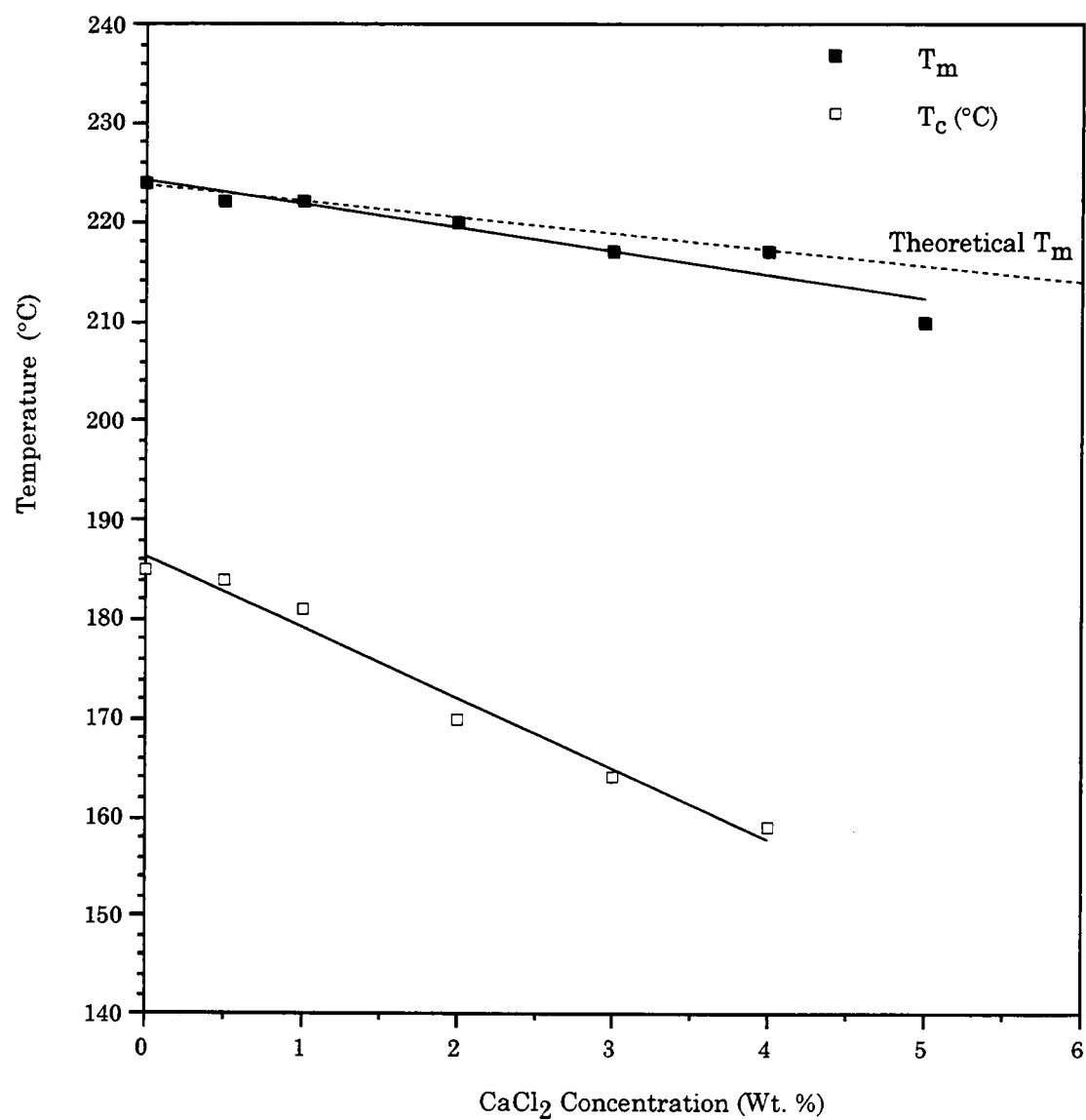


Figure 42. Melting and crystallization temperature depression for CaCl₂ blends.

sensitivity of the DSC.

Crystallinity changes in these blends are determined from the assumption that a perfect nylon 6 crystal has an enthalpy of 45 cal/g, or 188.3 J/g. Although these particular melting enthalpies are only applicable for cooling rates of 20°C/min., they are noted as a qualitative comparison between samples and not as an indication of the mechanically tested materials. The values for crystallinity, χ_c , are shown in Table 10. From these calculation it is apparent that not a high degree of change is observed no matter the amount of salt. This may indicate that the type of crystal formed is different and not the actual amount of crystalline material.

Injection molded samples

Thermal data for the injection molded samples was focused primarily on the crystallinity changes as a function of the salt content. The acquired values were used later for comparison to crystallinity determinations using X-ray diffraction. Percent crystallinity values and the accompanying values for the crystalline melting enthalpy are given in Table 11. Consideration for changes in crystallinity must be made in comparison to those obtained under the controlled 20°C/min. cooling in the DSC. The injection molding process results in a slower cooling rate for specimens sectioned from the center of the samples.

Wide Angle X-ray Diffraction

The X-ray diffraction data includes calculations of crystallinity fractions for all observed phases; the amorphous phase, α -monoclinic phase (β -monoclinic as

Table 10. Crystallinity data for thermally normalized blends.

Material	ΔH_m (J/g)	Crystallinity, χ_c
As-received pellets	34	18
Solution - no salt	43	23
Precipitated polymer	54	29
0.5% HA	43	23
1.0% HA	45	24
5.0% HA	44	23
6.0% HA	43	23
10.0% HA	41	22
0.5% CaCl_2	41	22
1.0% CaCl_2	39	21
2.0% CaCl_2	41	22
3.0% CaCl_2	28	15
4.0% CaCl_2	40	21
5.0% CaCl_2	26	14
6.0% CaCl_2	not observed	

Table 11. Crystallinity data for injection molded samples.

Material	ΔH_m (J/g)	Crystallinity, χ_c
As-received pellets	70	37
Solution - no salt	67	36
0.5% HA	64	34
1.0% HA	61	32
5.0% HA	57	30
6.0% HA	61	32
10.0% HA	61	32
0.5% CaCl_2	60	32
1.0% CaCl_2	62	33
5.0% CaCl_2	41	22
6.0% CaCl_2	14	7

well), and γ phase. These peak positions correspond to 2θ values (crystal planes) of approximately 19° for the amorphous, $11^\circ(002)$, $20^\circ(200)$, and $23^\circ(202)$ for the monoclinic phases, and $21^\circ(001)/(20\bar{1})/(200)$ for the pseudo-hexagonal γ phase.

An example plot of the peak-fitting output is shown in Figure 43. In addition to this information the program outputs a data summary which lists all curve-fitting coefficients, measured values, etc. In determining the phase content crystallinity measurements from the DSC were used as a guide in determining an appropriate fit for the amorphous background curve. All samples with their respective phase contents are shown in Table 12. The Gaussian equation is used for analysis of the amorphous content and the Pearson equation for the crystalline fractions. The analysis was performed so as to attain an R^2 value of at least 0.99. This results in a standard of error of less than $\pm 2.0\%$ for all sample percentages.

Phase content in the dry hydroxyapatite blended polymers did not change significantly. This is not the case for the conditioned hydroxyapatite blends in which the crystalline fraction of the pseudo-hexagonal γ phase were reduced. Comparison plots for these dry and conditioned samples are shown in Figures 44 and 45.

Dry and conditioned blends of CaCl_2 (Figures 46 and 47) have considerable changes between the low and high concentrations of salt. The crystalline structure is completely transformed into an amorphous curve at the higher concentrations. Slight shifts in the remaining peak positions are also noted, indicating a possible change in the separation between the remaining crystalline entities.

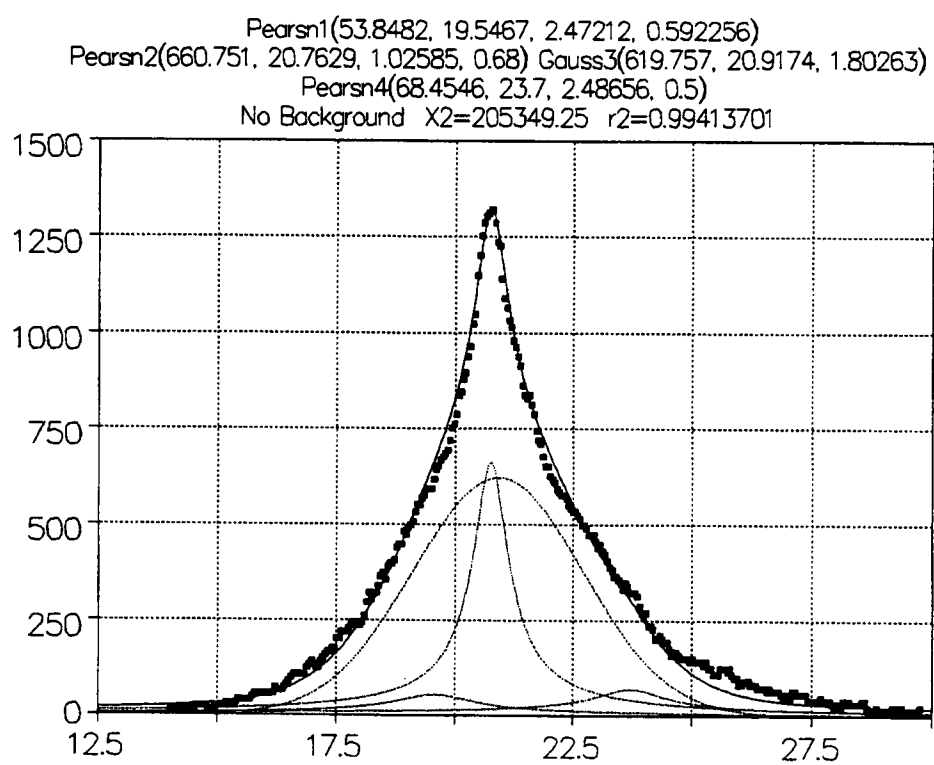


Figure 43. Example figure of peak-fitting output for x-ray analysis.

Table 12. X-ray crystallographic data for all blends.

Material	Gaussian Peak #1, (% Area)	Gaussian Peak #2, (% Area)	Pearson Peak #1, (% Area)	Pearson Peak #2, (% Area)	Pearson Peak #3, (% Area)
Dry pellets	21.2 (61%)	N/A	21.0 (39%)	N/A	N/A
Dry 0.0% solution	21.3 (58%)	N/A	21.2 (23%)	23.2 (16%)	19.5 (3%)
Dry 0.5% HA	21.4 (67%)	N/A	21.3 (26%)	23.6 (7%)	N/A
Dry 1.0% HA	20.9 (61%)	N/A	20.7 (27%)	23.7 (7%)	19.5 (5%)
Dry 5.0% HA	21.6 (56%)	N/A	21.2 (38%)	22.1 (5%)	19.7 (1%)
Dry 6.0% HA	21.3 (59%)	25.8 (2%)	20.9 (36%)	22.8 (2%)	19.2 (1%)
Dry 10.0% HA	21.2 (63%)	N/A	20.5 (29%)	22.1 (3%)	19.1 (5%)
Dry 0.5% CaCl ₂	21.6 (64%)	N/A	21.2 (31%)	23.4 (1.6%)	19.7 (2.4%)
Dry 1.0% CaCl ₂	21.4 (65%)	26.8 (5%)	21.2 (30%)	N/A	N/A
Dry 5.0% CaCl ₂	22.2 (87%)	29.4 (6%)	21.7 (7%)	N/A	N/A
Dry 6.0% CaCl ₂	21.0 (70%)	26.4 (23%)	20.6 (7%)	N/A	N/A
"Wet" pellets	21.4 (51%)	N/A	21.1. (49%)	N/A	N/A
"Wet" 0.0%	21.6 (57%)	N/A	21.3 (38%)	22.3 (4%)	19.3 (1%)
"Wet" 0.5% HA	21.7 (63%)	N/A	21.1 (28%)	22.8 (4%)	19.8 (5%)
"Wet" 1.0% HA	21.4 (59%)	N/A	20.9 (35%)	23.1 (4%)	19.2 (2%)
"Wet" 5.0% HA	21.7 (57%)	N/A	21.3 (32%)	23.6 (3%)	20.1 (3%)
"Wet" 6.0% HA	21.4 (66%)	N/A	21.2 (21%)	23.7 (8%)	18.3 (5%)
"Wet" 10.0% HA	21.5 (70%)	N/A	21.2 (21%)	23.4 (4%)	20.0 (5%)
"Wet" 0.5% CaCl ₂	21.9 (57%)	N/A	21.2 (35%)	22.7 (4%)	19.5 (4%)
"Wet" 1.0% CaCl ₂	21.6 (69%)	N/A	21.1 (21%)	22.4 (6%)	19.9 (4%)
"Wet" 5.0% CaCl ₂	20.7 (73%)	25.0 (23%)	20.2 (4%)	N/A	N/A
"Wet" 6.0% CaCl ₂	20.0 (82%)	24.4 (18%)	N/A	N/A	N/A

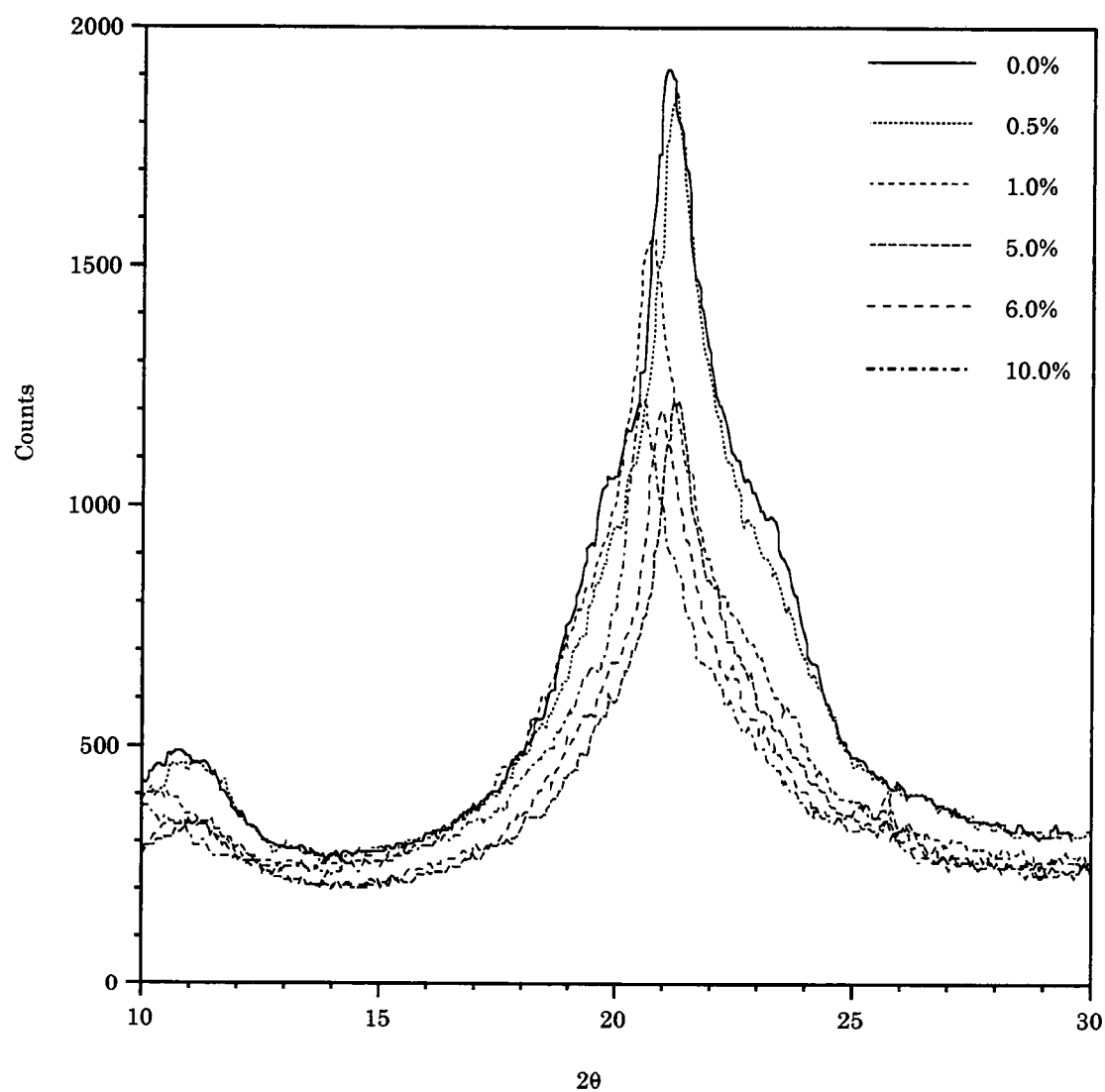


Figure 44. Crystallographic scans of dry hydroxyapatite blends.

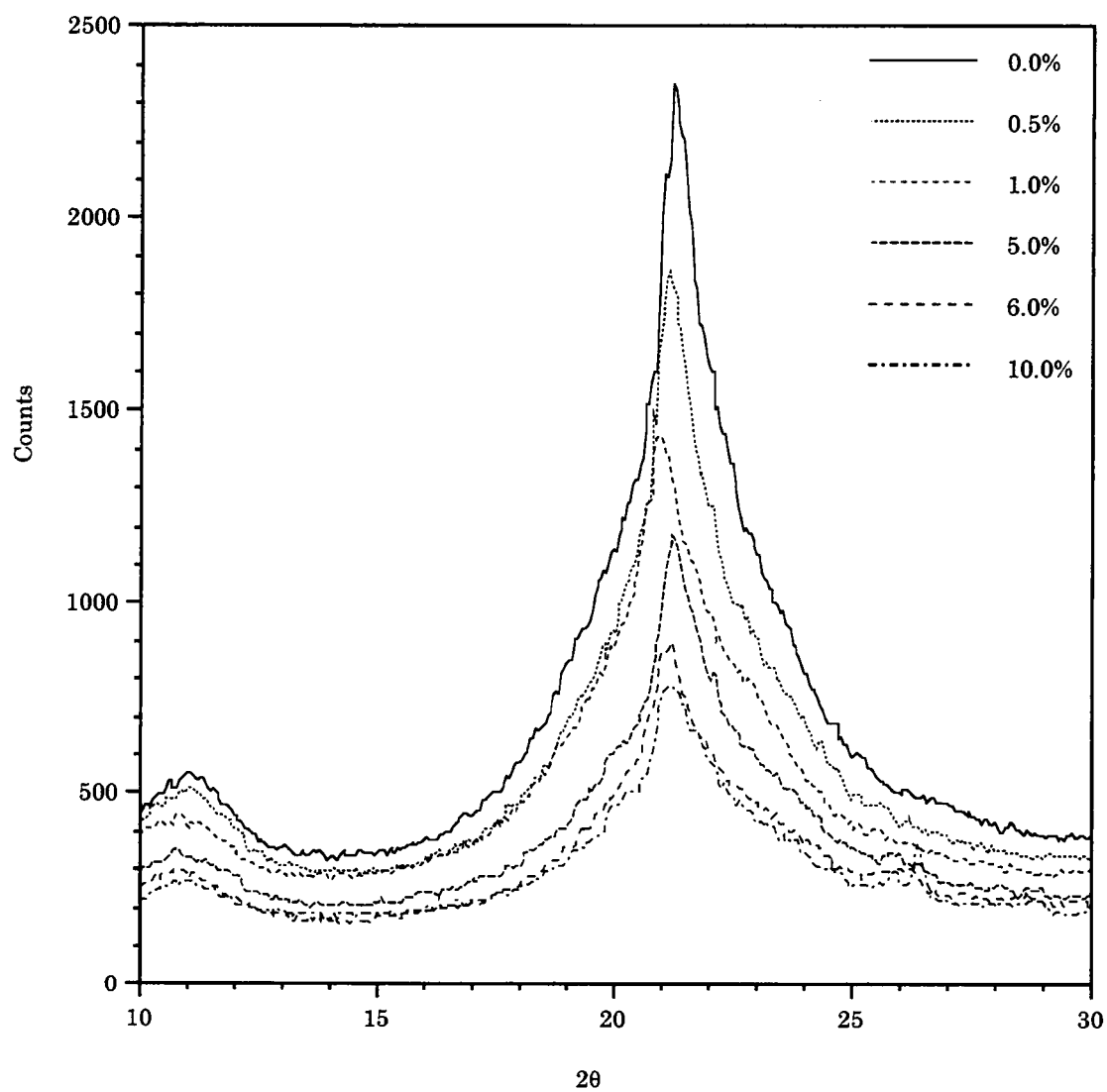


Figure 45. Crystallographic scans of conditioned hydroxyapatite blends.

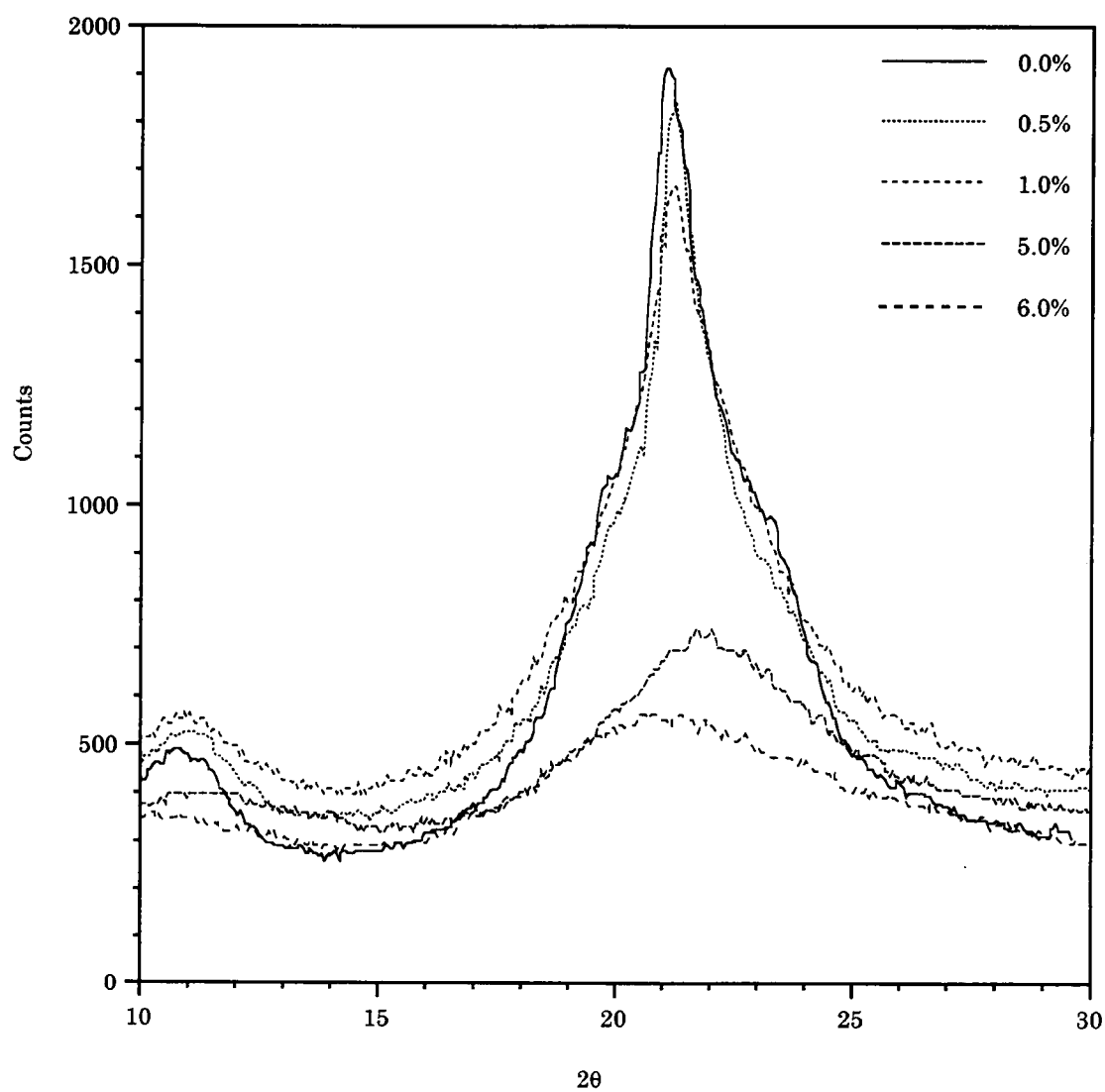


Figure 46. Crystallographic scans of dry CaCl_2 blends.

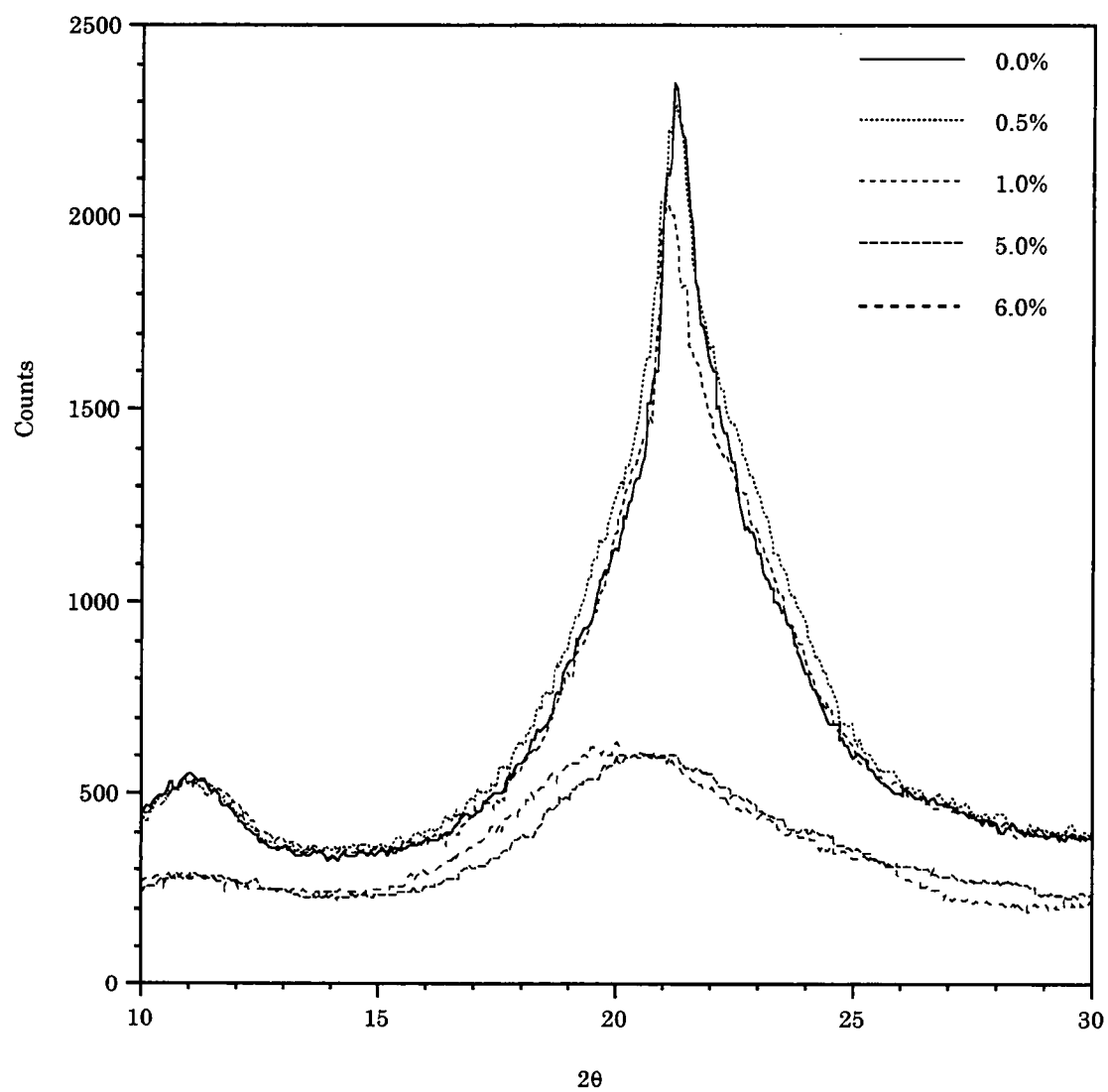


Figure 47. Crystallographic scans of conditioned CaCl_2 blends.

Fourier Transform Infrared Spectroscopy

The confirmation of crystallinity changes by FT-IR in the thin film blends is shown in Figures 48 and 49 for the hydroxyapatite and CaCl_2 blends respectively. A qualitative comparison can be made directly between the changes in crystalline phases with the addition of either salt. The hydroxyapatite blends showed minimal changes in the crystalline sensitive bands as well as the C-CO stretching band. If the intensity of the C-CO band decreases it is an indication that an increase in the hydrogen bonding on the polymer main chain has taken place.

Large changes are observed with the addition of salt for all crystalline sensitive bands in the CaCl_2 blends. Crystalline absorption bands for the γ phase drop until hardly observable. As well there is a decrease in the intensity of the C-CO stretching absorption bands.

Differentiation of the carbonyl group for all blends can be observed in Figures 50 and 51. The results indicate significant changes in the CaCl_2 blends. These changes are manifested in the unassociated carbonyl absorbance band. In addition to a decrease in intensity there also exists a shift in the relative position of the band, an indication of an increase hindrance in movement by some factor attributable to the addition of CaCl_2 salt. Hydroxyapatite blends show a minimal decrease in the unassociated carbonyl band, however there is a slight change in the Amide I, C=O stretching band. Increased restriction of this molecular group is indicated by a shift in the band at 1648 cm^{-1} . Changes of this type for the associated carbonyl may indicate a possible increase in the order of the crystalline phase, namely a shift from the β -monoclinic to the α -monoclinic, or slight hindrance of the "ordered" amorphous phase due to the particulates.

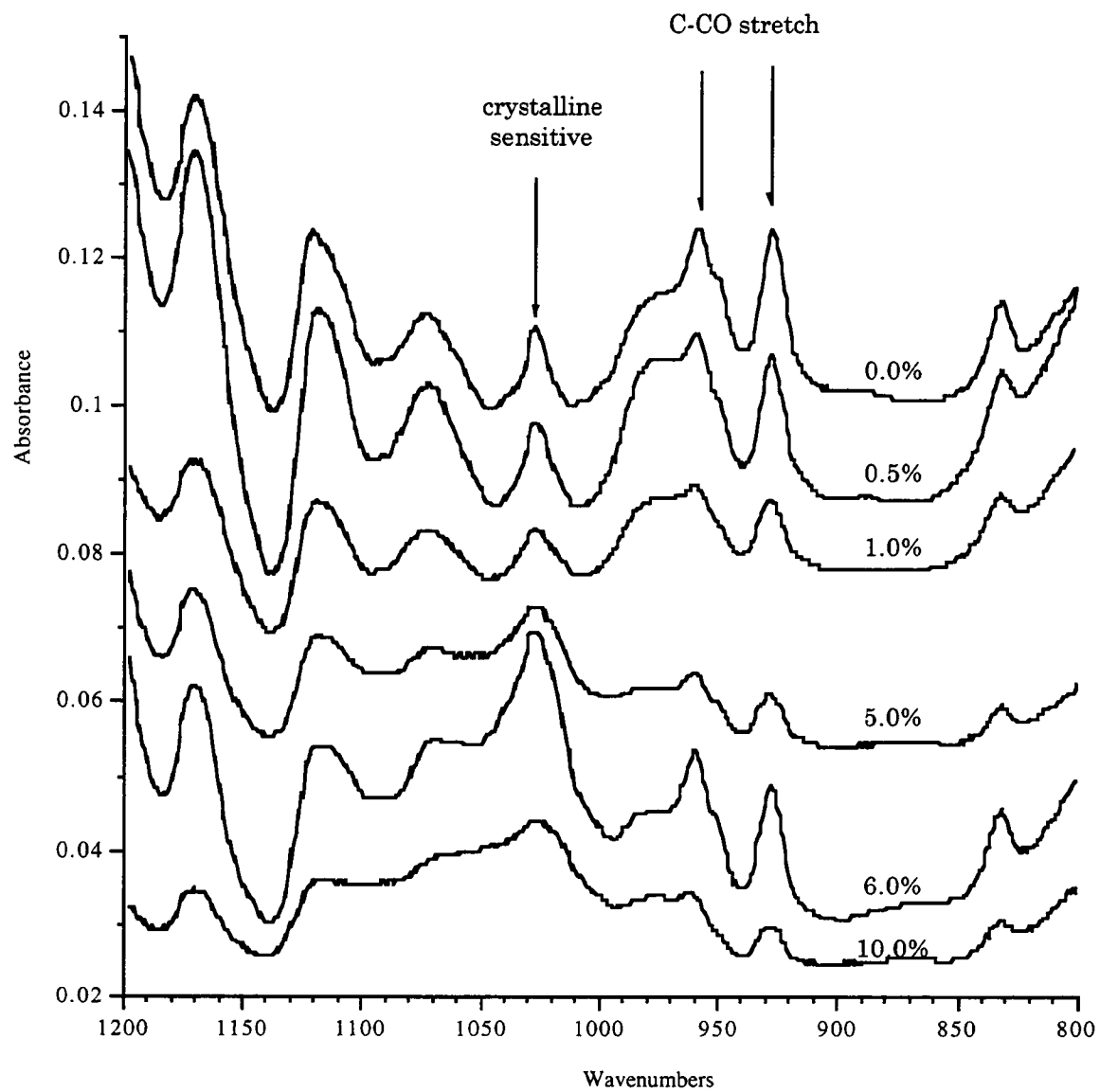


Figure 48. Crystalline peak comparisons by FT-IR for hydroxyapatite blends.

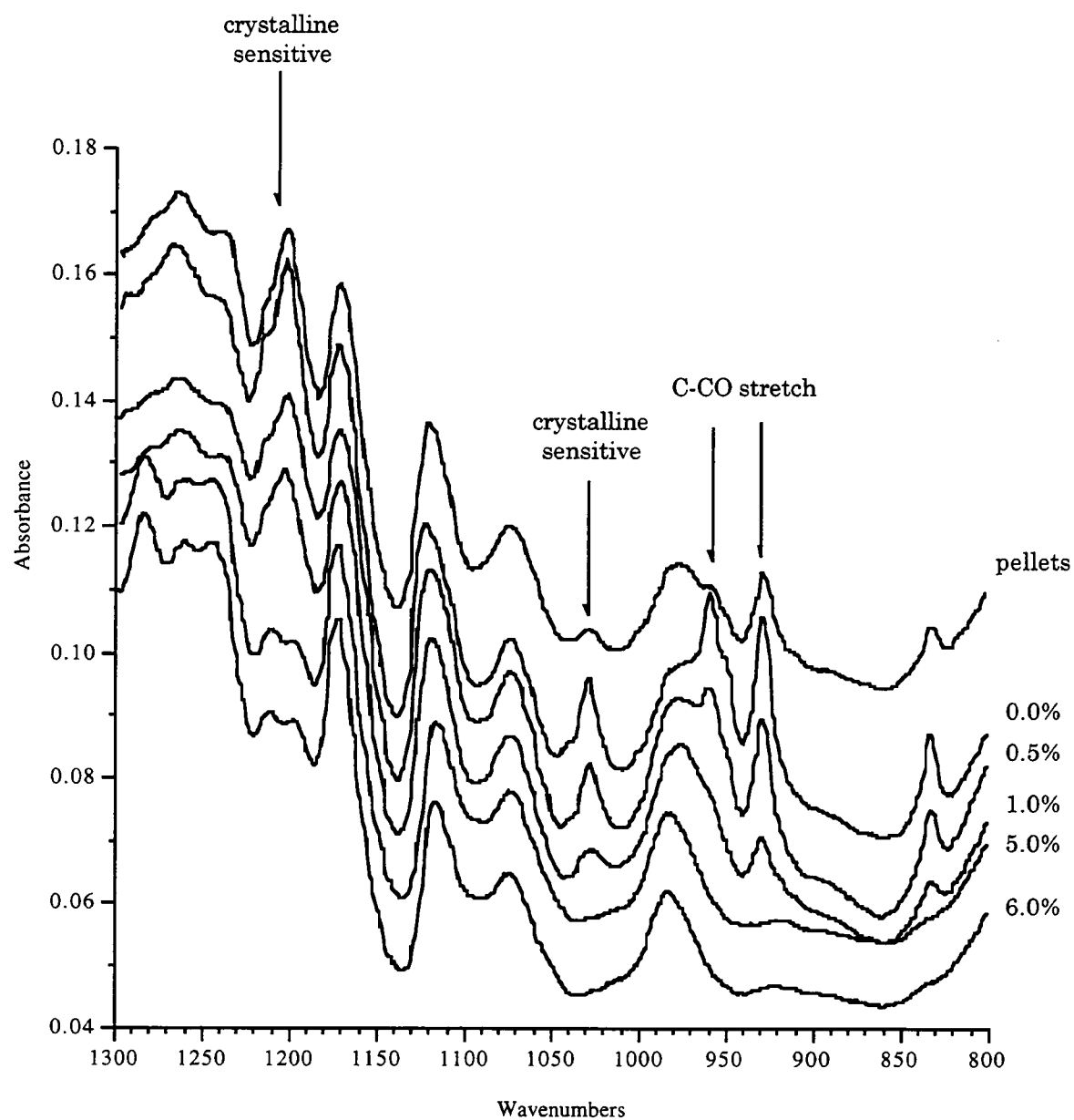


Figure 49. Crystalline peak comparisons by FT-IR for CaCl₂ blends.

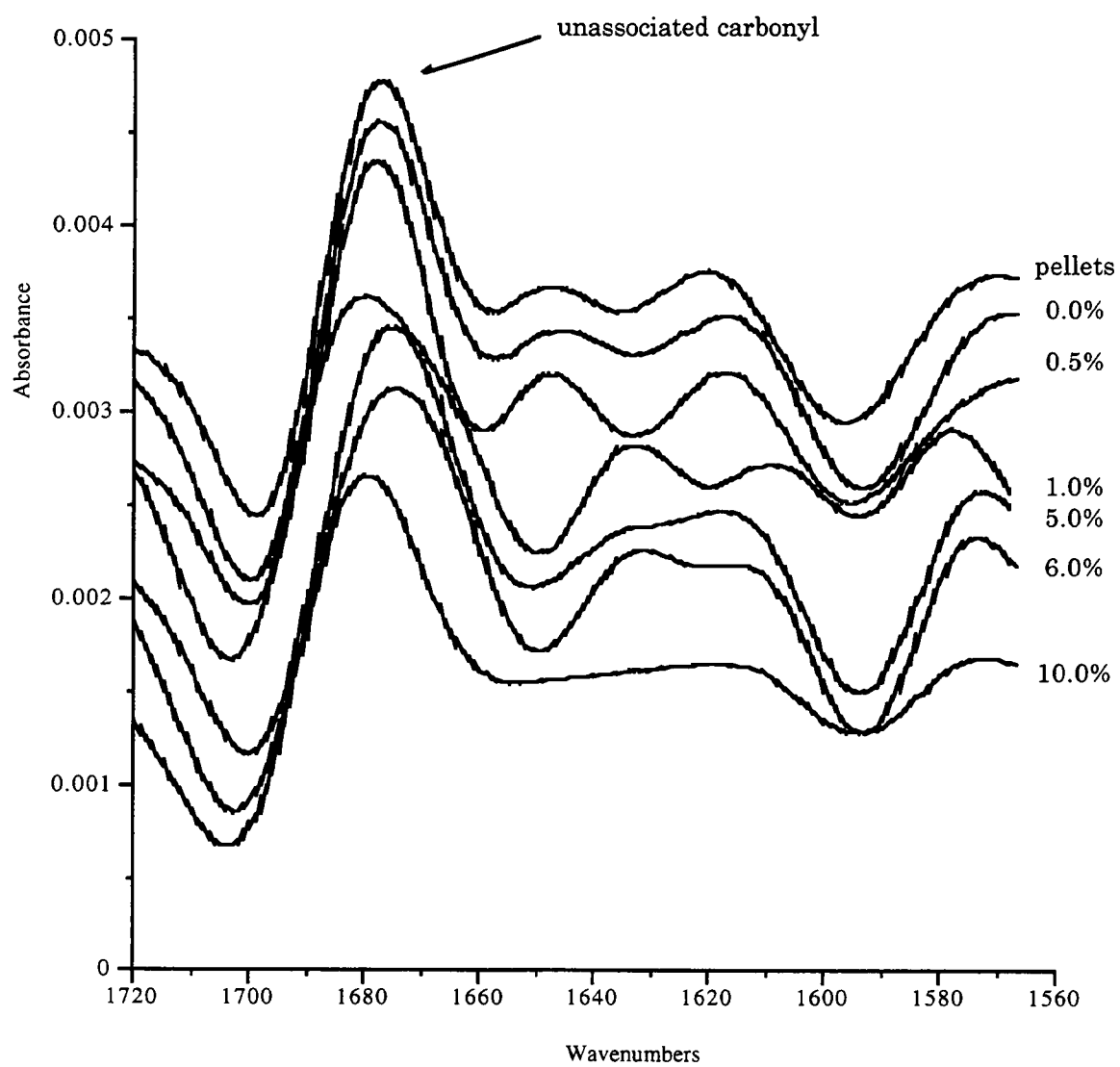


Figure 50. Differentiation of carbonyl groups on hydroxyapatite blends.

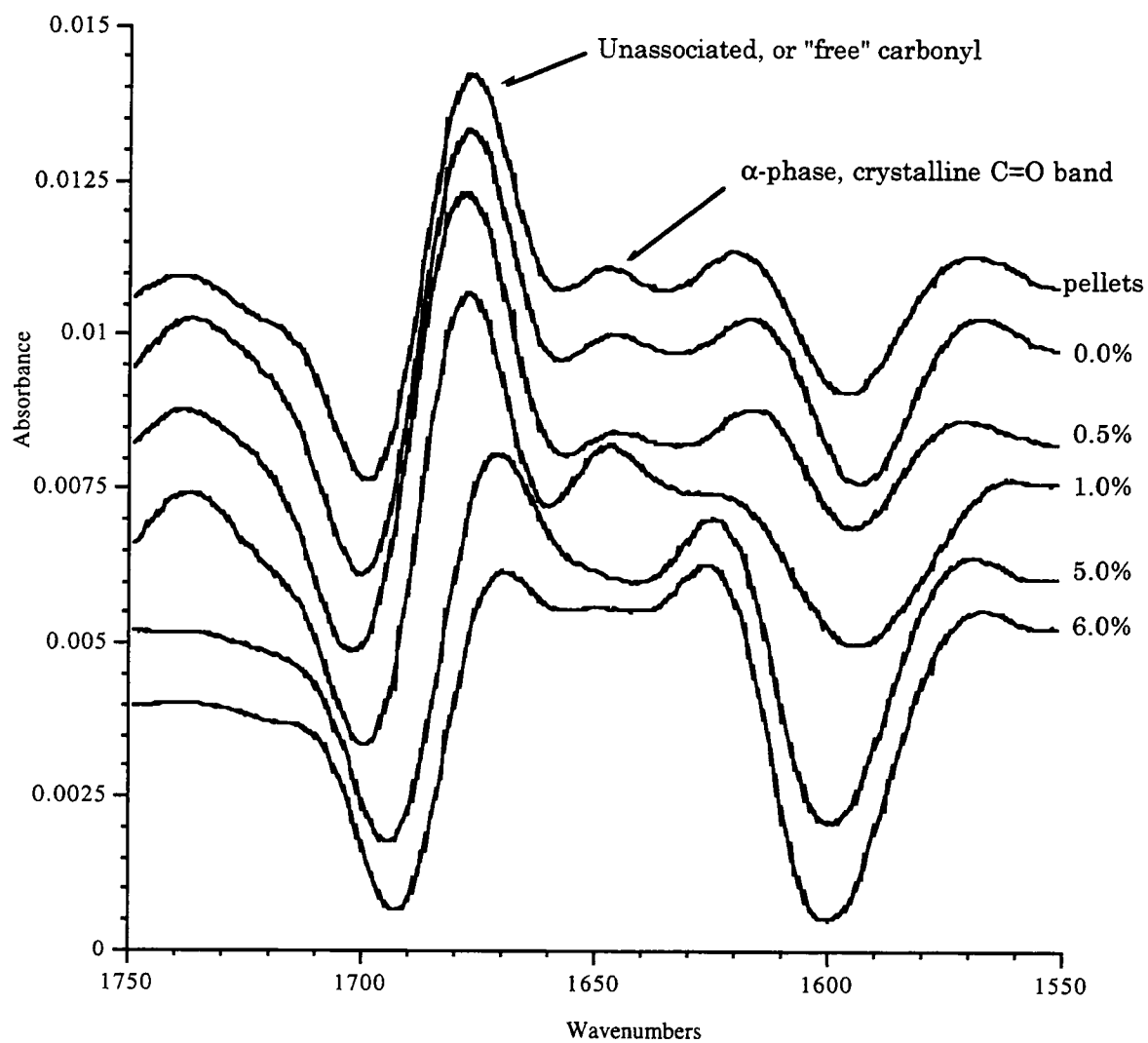


Figure 51. Differentiation of carbonyl groups on CaCl_2 blends.

ATR results were used mainly to observe the effects of moisture uptake on the functional groups of the polyamide. The plasticizing due to the water is observed to increase the mobility of the CH_2 groups in particular. The role this plays on the mechanical properties will be discussed in relation to the presented tensile data.

Dynamic Mechanical Analysis

The internal damping friction, or $\tan \delta$ for the dry and conditioned hydroxyapatite blends are shown in Figures 52 and 53. There is little change between the temperature of maximum loss for the 0.0% solution sample and that of the 10.0% hydroxyapatite. However, in the process of attaining the same transition temperature, there is an increase in the peak with increasing concentration. The peak reaches a maximum of 83°C at the 6.0% blend, dropping back to 67°C in the 10.0% sample. This overall temperature shift is approximately 16°C .

A true measure of the T_g requires analysis of the loss modulus (E'') for these samples. These curves are shown in Figures 54 and 55 for both sets of hydroxyapatite blends. This shift to a higher temperature is also approximately 16°C . The change suggests some chain hindrance due to incorporation of the $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ salt. Glass transitions for all blends, hydroxyapatite and CaCl_2 are displayed in Table 13.

Internal damping losses in CaCl_2 blends show dramatic changes at elevated temperatures. There is an indication of a secondary glass transition temperature. The exact nature of this significant change will be discussed later in this paper. This

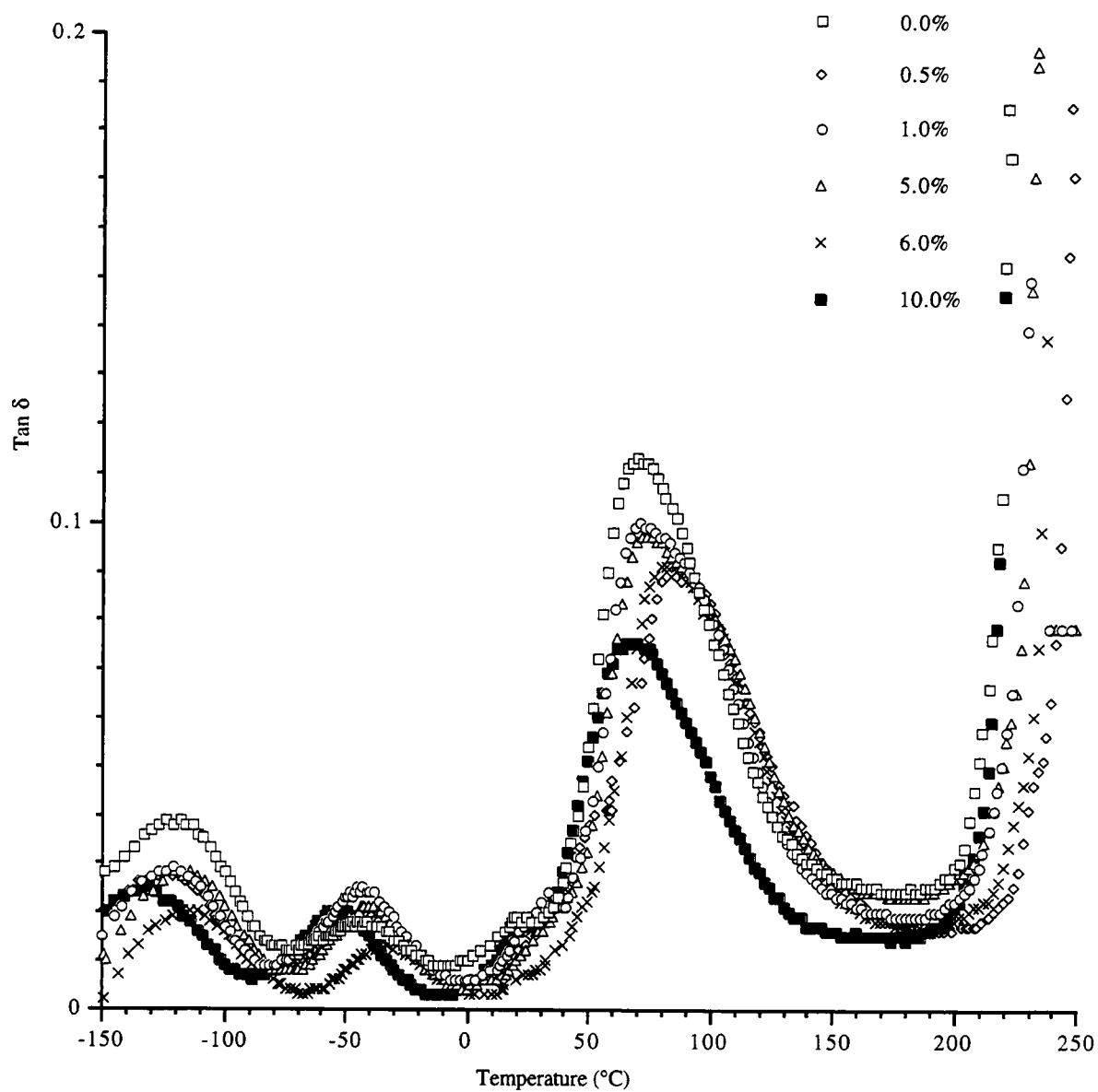


Figure 52. Internal damping ($\tan \delta$) of dry hydroxyapatite blends.

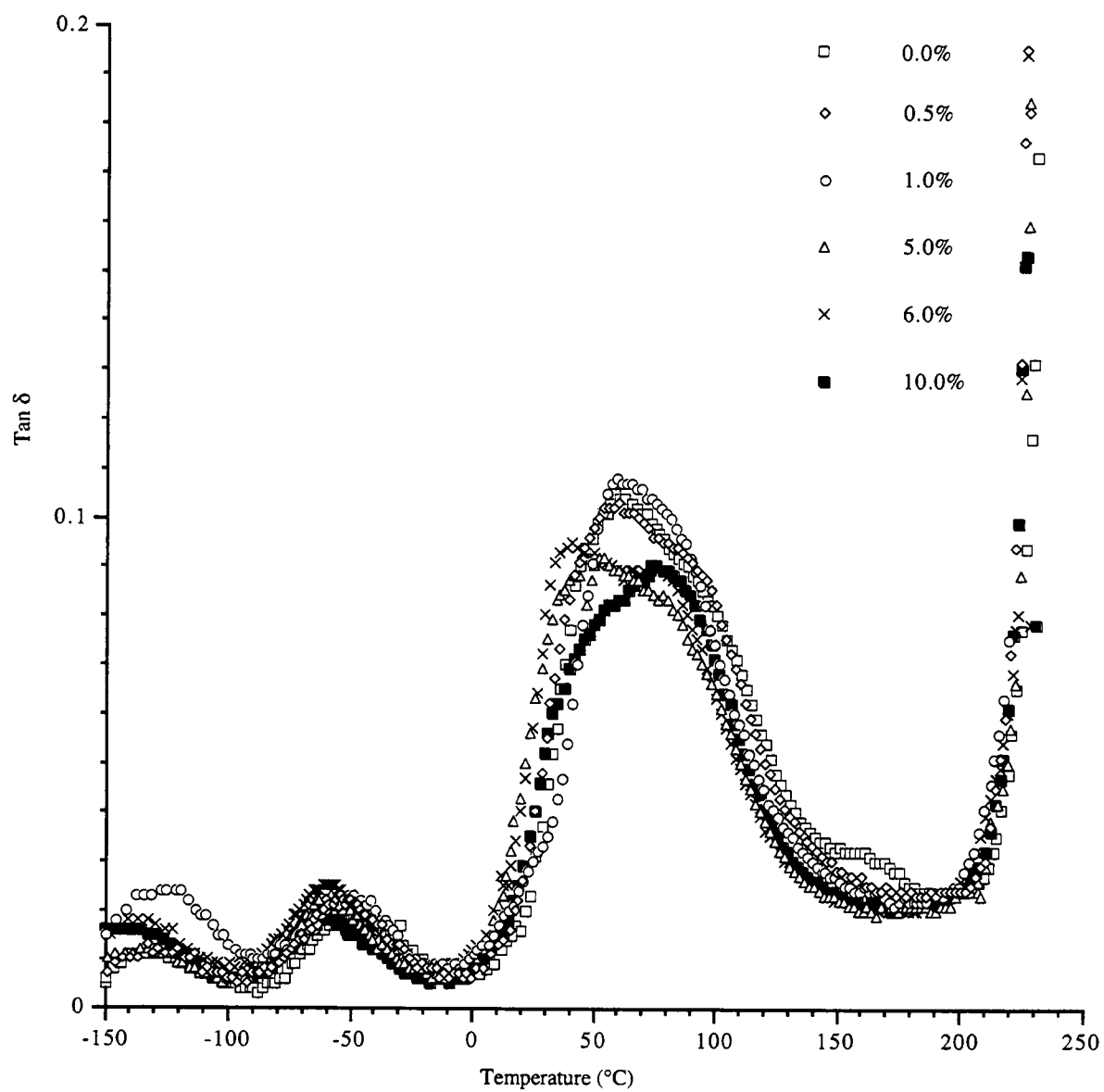


Figure 53. Internal damping ($\tan \delta$) of conditioned hydroxyapatite blends.

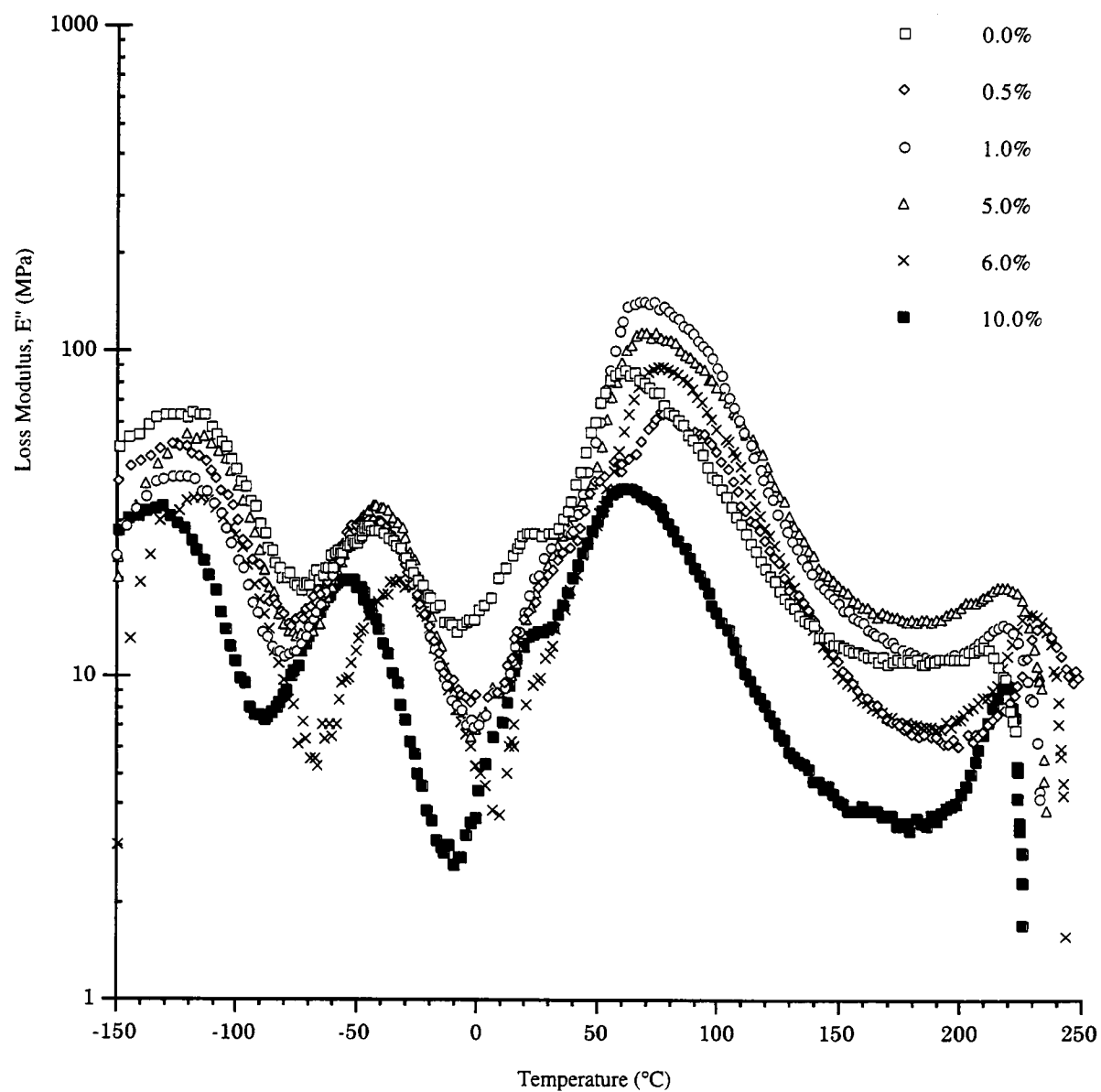


Figure 54. Loss modulus (E'') for dry hydroxyapatite blends.

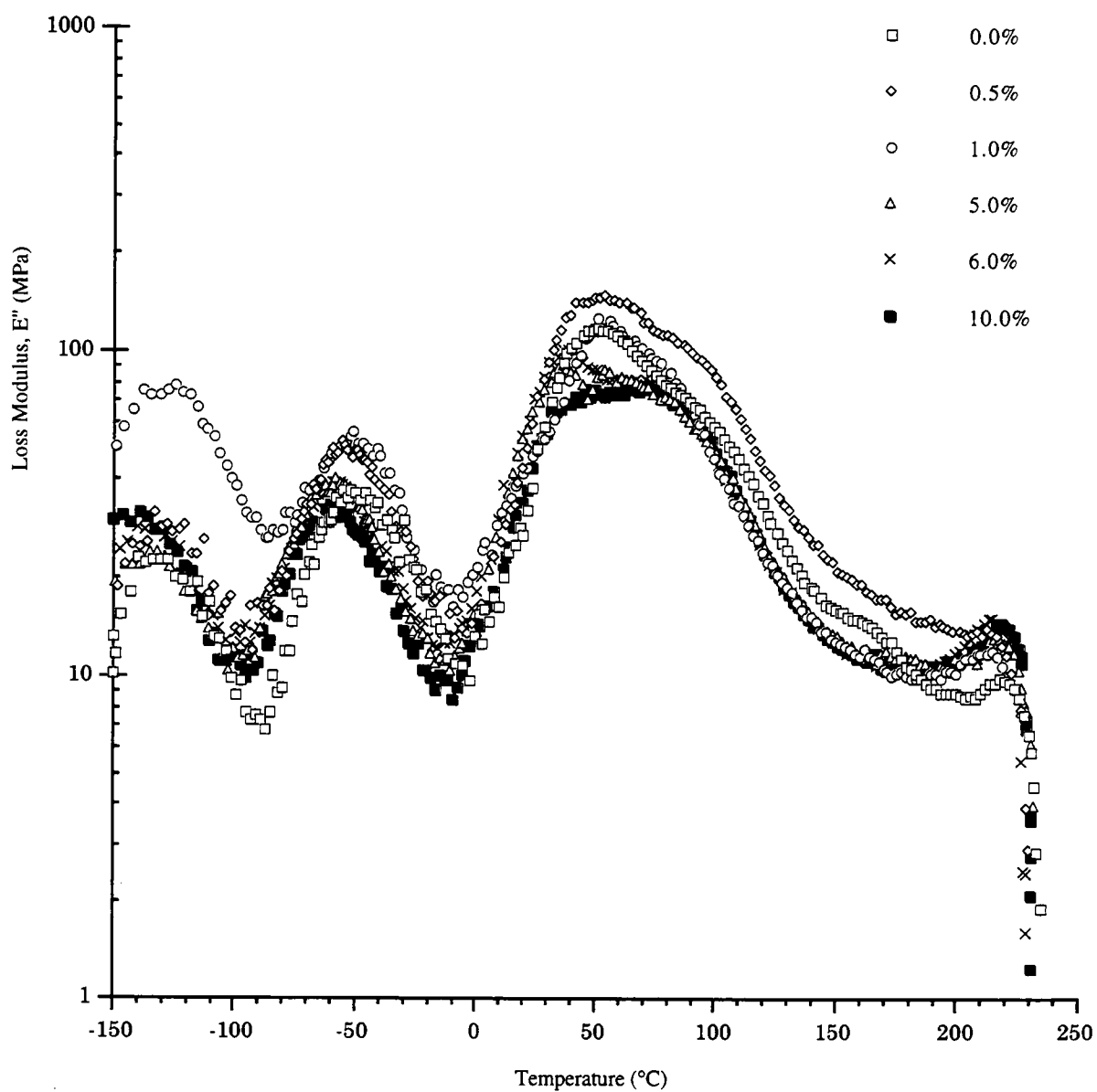


Figure 55. Loss modulus (E'') for conditioned hydroxyapatite blends.

Table 13. Glass transition temperatures for all blends as determined by DMA.

Material	Primary T_g (°C)	Secondary T_g (°C)
dry solution	61	N/A
0.5% dry HA	76	N/A
1.0% dry HA	68	N/A
5.0% dry HA	70	N/A
6.0% dry HA	77	N/A
10.0% dry HA	65	N/A
0.5% dry CaCl_2	60	N/A
1.0% dry CaCl_2	70	N/A
5.0% dry CaCl_2	68	139
6.0% dry CaCl_2	73	139
conditioned solution	62	N/A
conditioned 0.5% HA	67	N/A
conditioned 1.0% HA	61	N/A
conditioned 5.0% HA	62	N/A
conditioned 6.0% HA	62	N/A
conditioned 10.0% HA	63	N/A
conditioned 0.5% CaCl_2	65	N/A
conditioned 1.0% CaCl_2	67	N/A
conditioned 5.0% CaCl_2	76	132
conditioned 6.0% CaCl_2	62	132

transition is illustrated in both the loss modulus and $\tan \delta$ plots for dry and conditioned states as shown in Figures 56-59.

The hydroxyapatite blends did not exhibit significant storage modulus changes, however, the CaCl_2 blends showed significant transitions. The plots of storage modulus versus temperature for dry and conditioned CaCl_2 blends are shown in Figures 60 and 61. There is a significant transition that becomes apparent at higher concentrations of salt. The increase in storage modulus at this point suggests supplementary reinforcement of the modulus at 132°C or as an indication of a secondary glass transition. Causes for this may stem from the high level of molecular interaction of the Ca^{++} ions with the amorphous chains.

The storage modulus curves for the hydroxyapatite blends are shown in Figures 62 and 63. Essentially, little change is found over the entire temperature range with an increase in filler content. One can conclude that little reinforcement of the amorphous polymer matrix is taking place.

Notched Izod Impact

As predicted from the equations proposed by Kerner the impact resistance of the materials decreased with an increase in filler content. This phenomena is illustrated in Figure 64 along with the Kerner predictions. In the case of the hydroxyapatite blends the decrease was due to the void formation around the particulates. These act as stress risers and have a detrimental consequence on the energy absorbed by the material. Impact results are listed in Table 14 in terms of energy absorption capacity, or in.-lb./in.³.

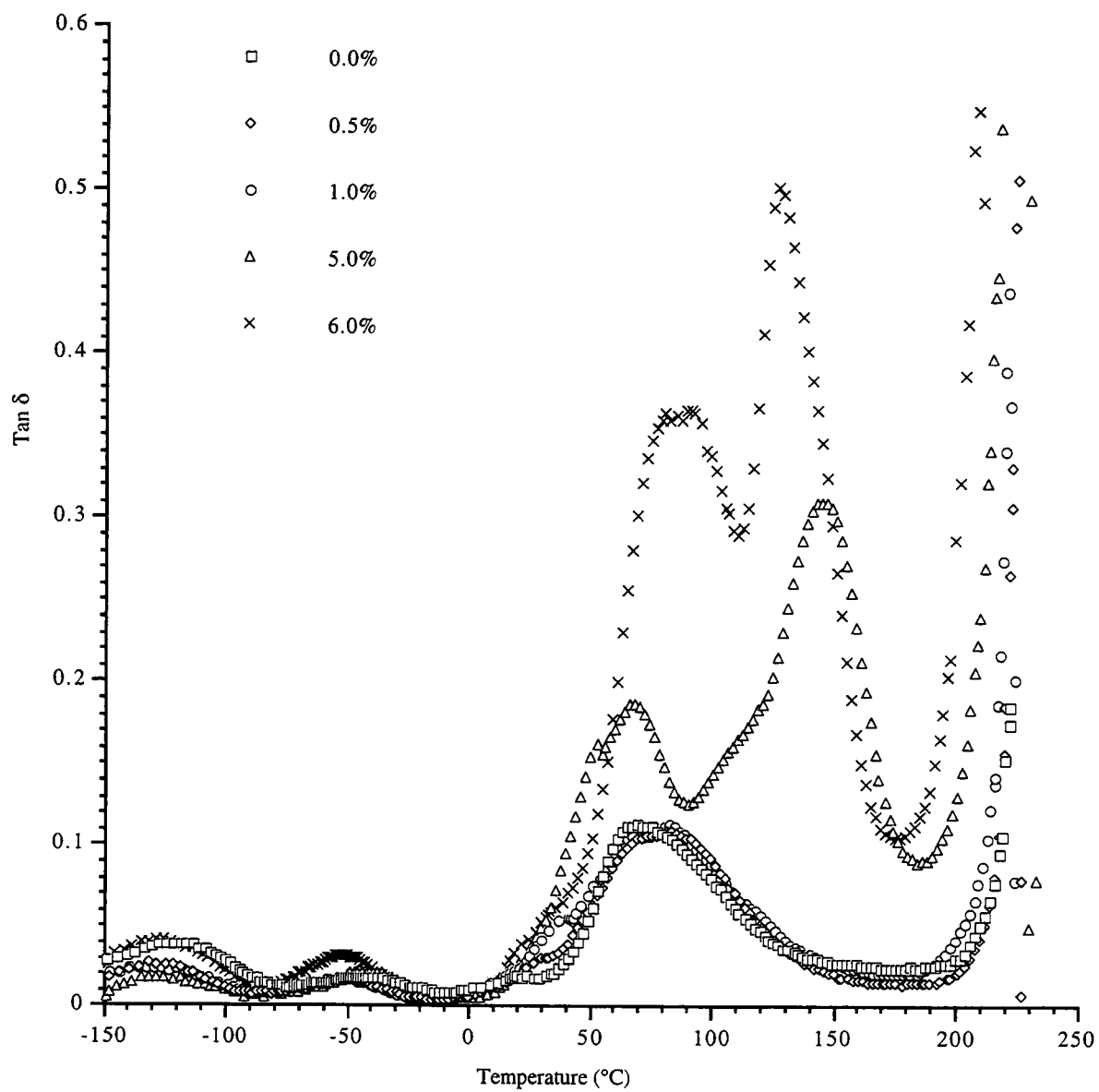


Figure 56. Internal damping ($\tan \delta$) of dry CaCl_2 blends.

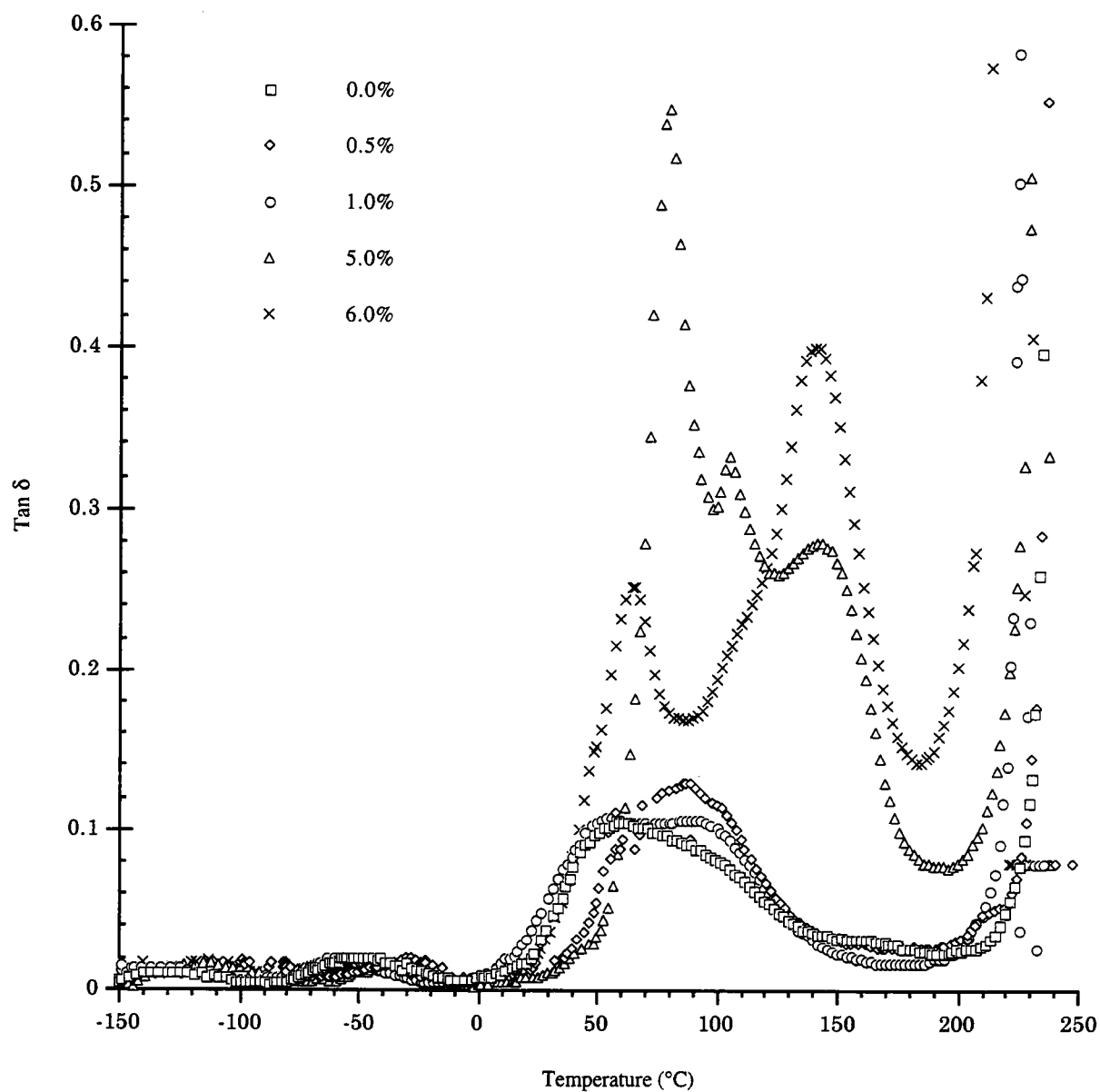


Figure 57. Internal damping ($\tan \delta$) of conditioned CaCl_2 blends.

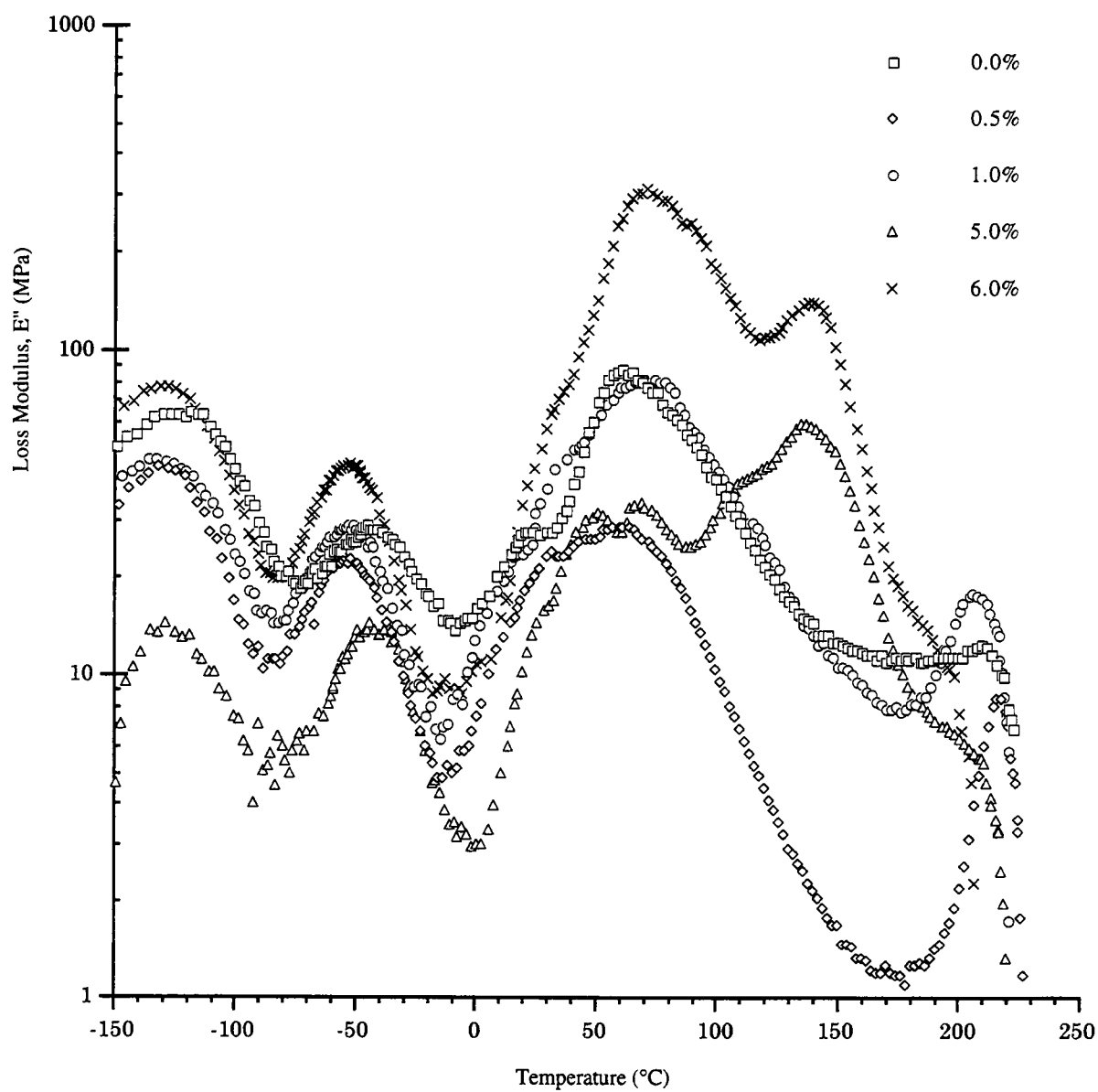


Figure 58. Loss modulus (E'') for dry CaCl_2 blends.

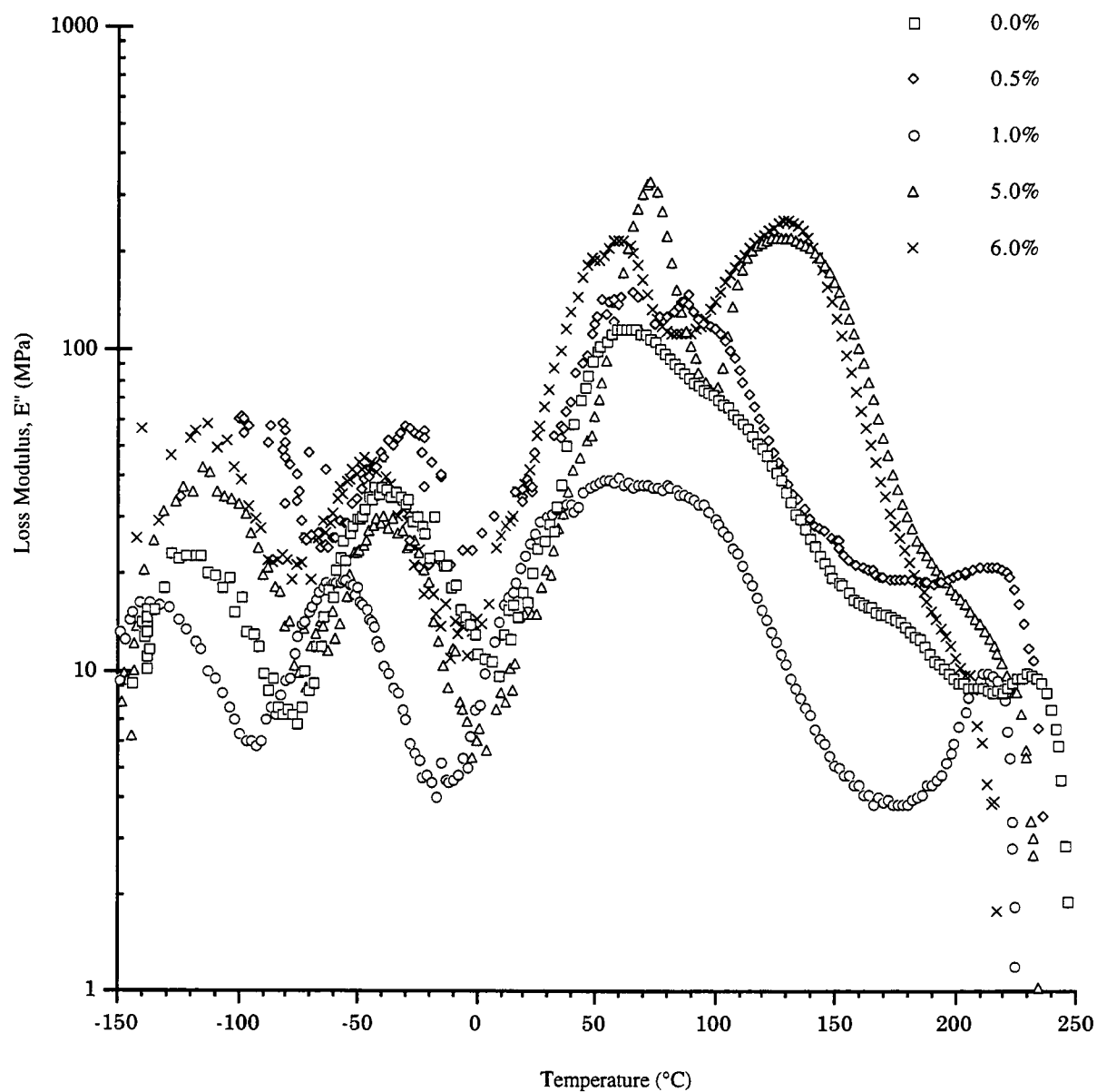


Figure 59. Loss modulus (E'') for conditioned CaCl_2 blends.

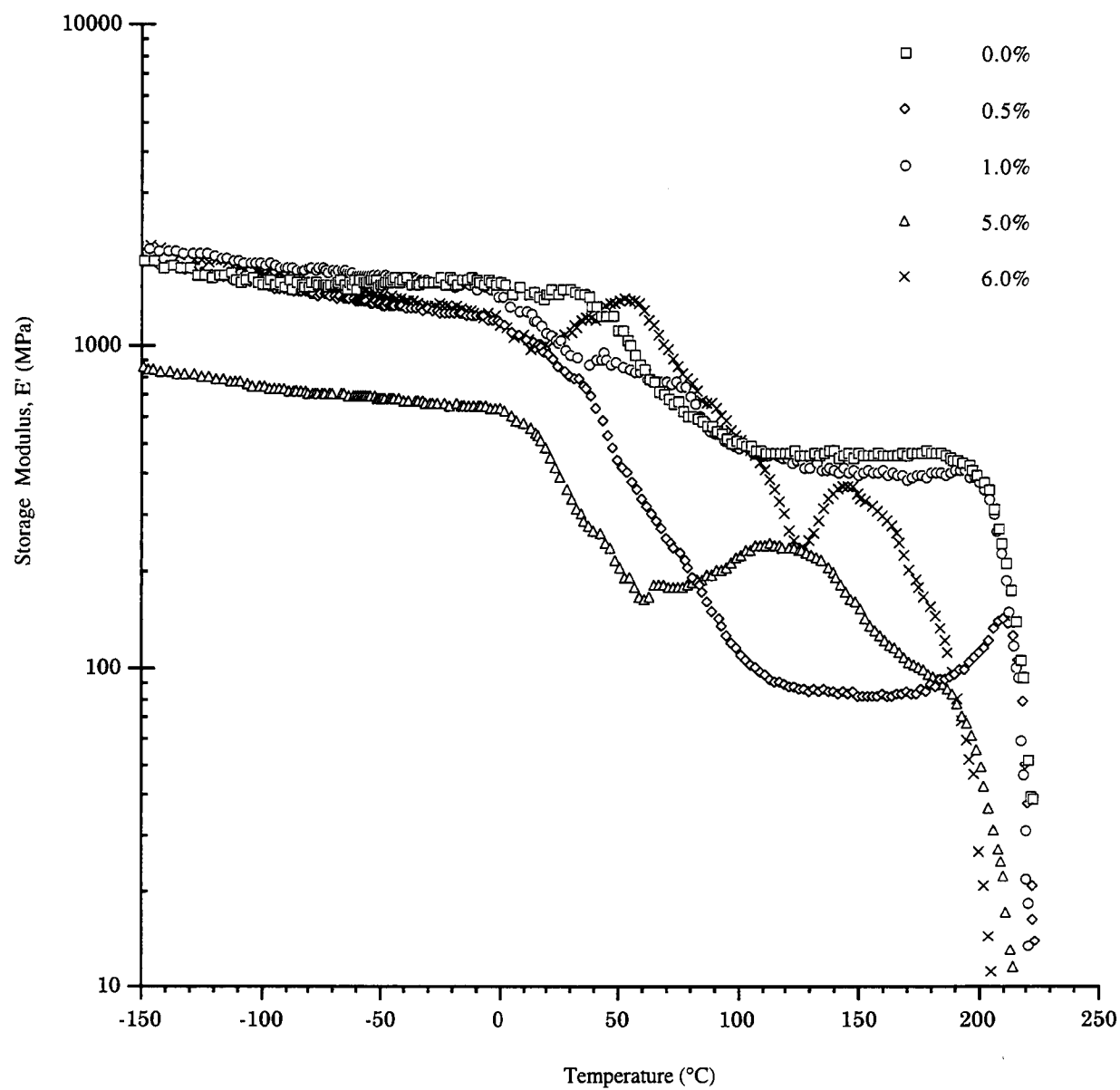


Figure 60. Storage modulus (E') for dry CaCl_2 blends.

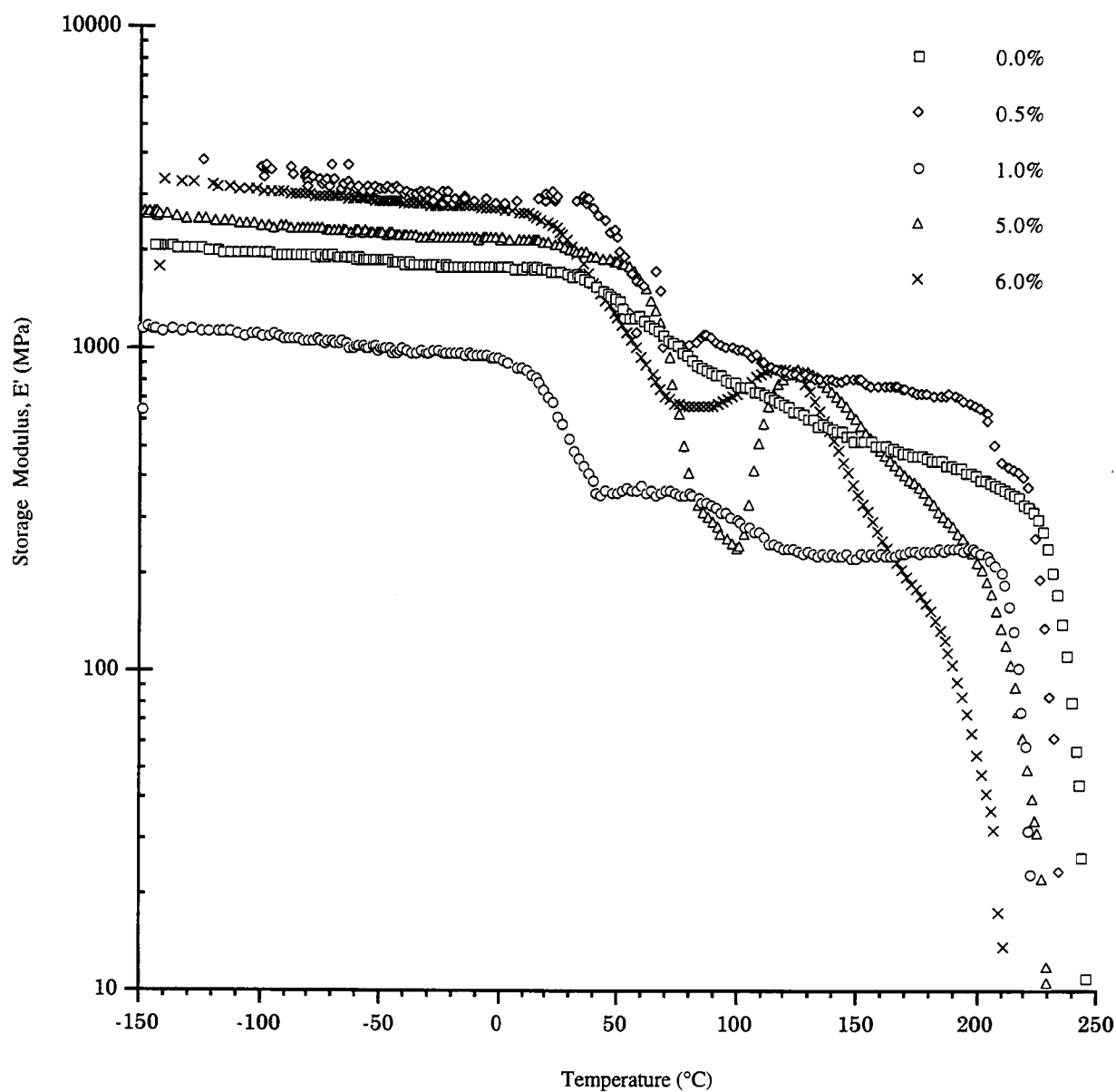


Figure 61. Storage modulus (E') for conditioned CaCl_2 blends.

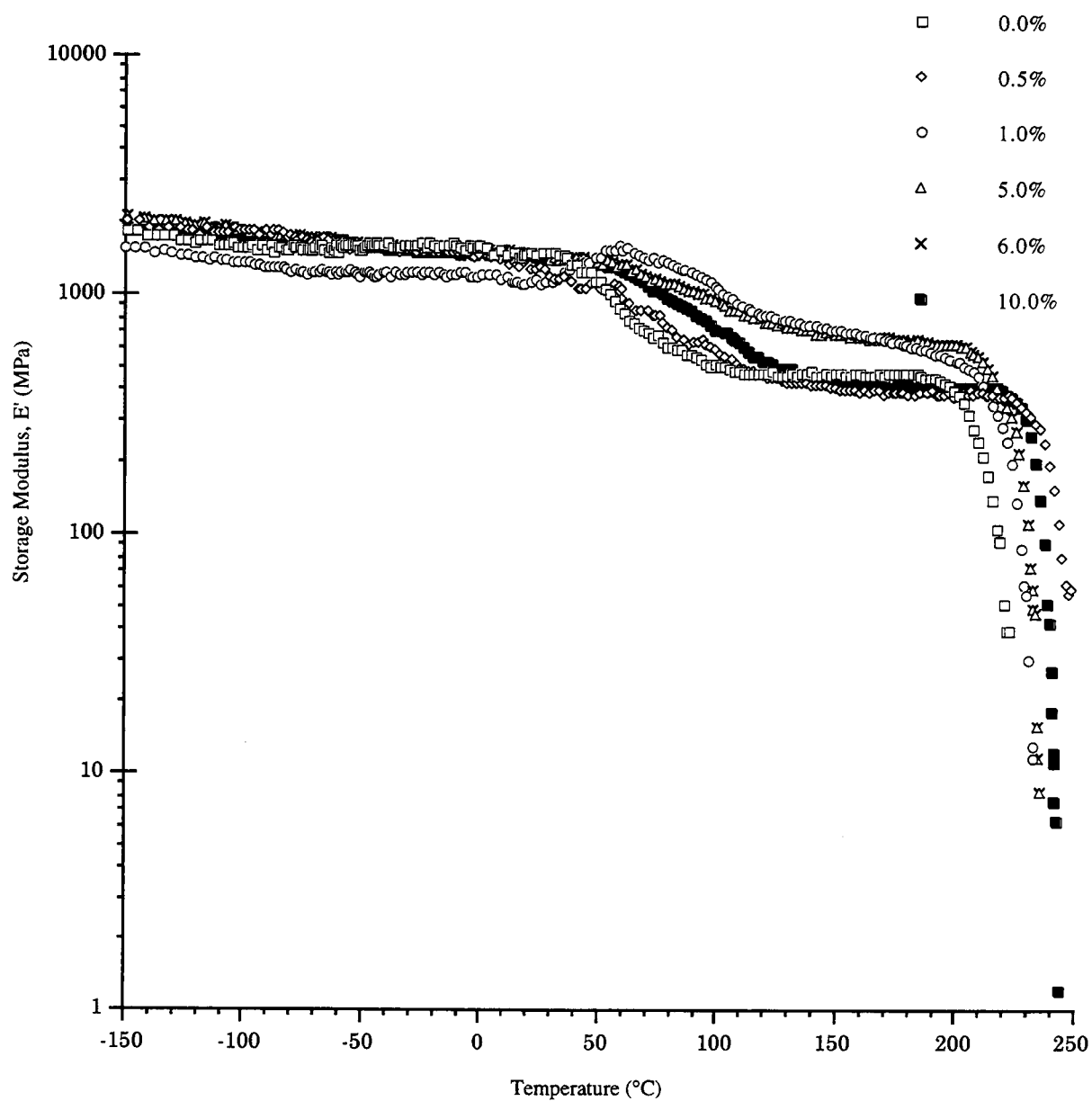


Figure 62. Storage modulus (E') for dry hydroxyapatite blends.

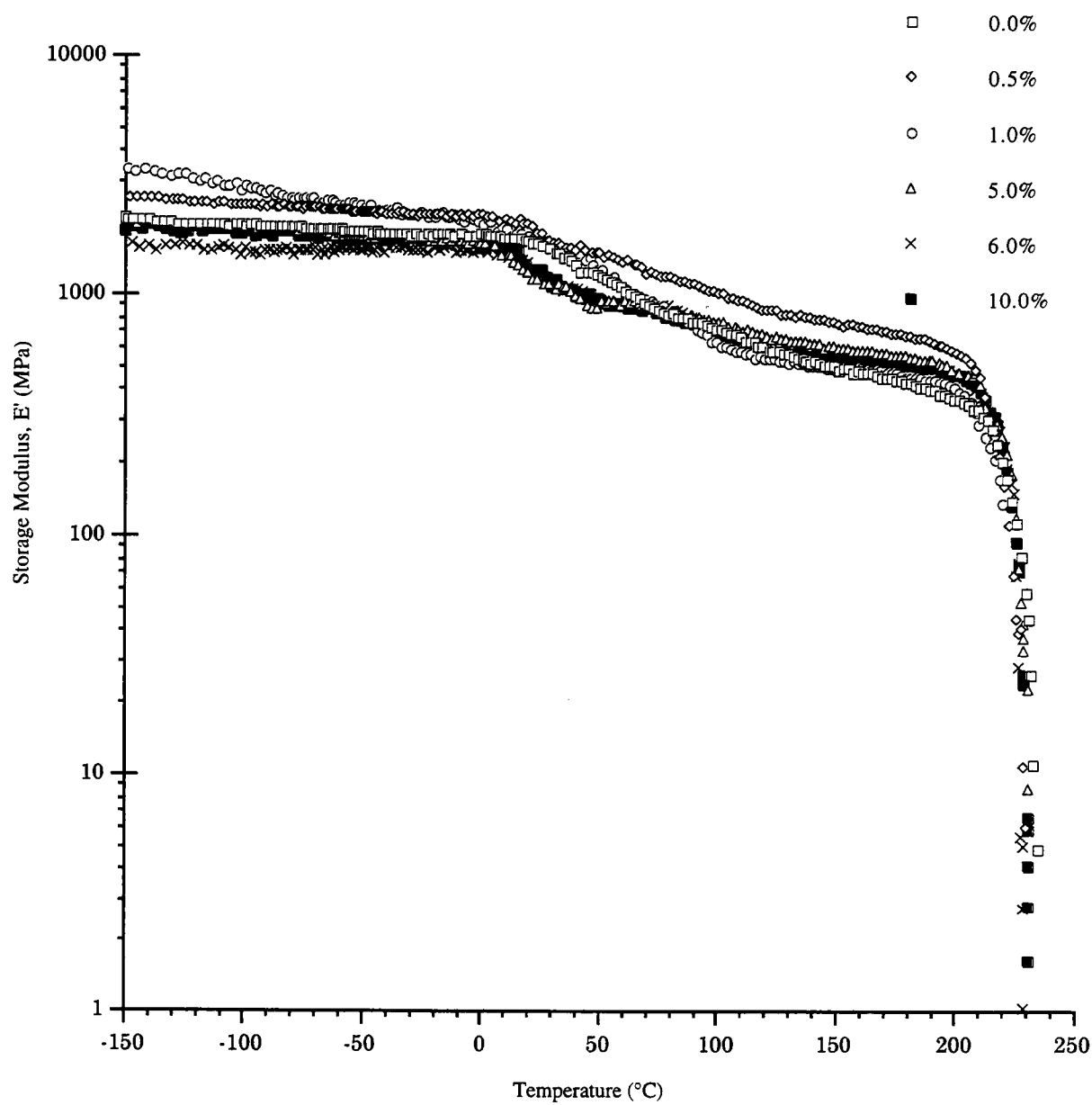


Figure 63. Storage modulus (E') for conditioned hydroxyapatite blends.

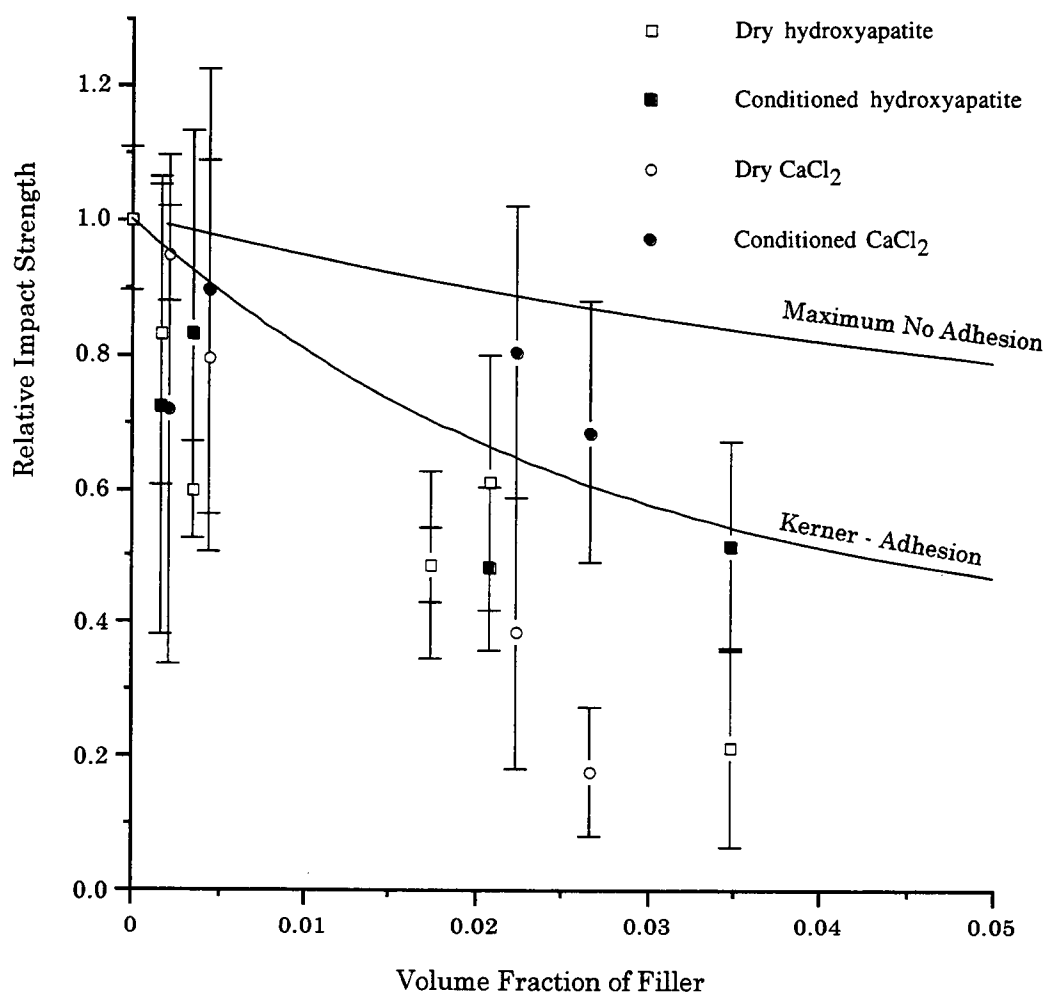


Figure 64. Izod impact results with Kerner prediction.

Table 14. Izod impact results for all molded samples.

Material	Energy-absorption (in.-lb./in. ³)
Embalsmed femur[77](McElhaney)	260
dry from pellets	181 ± 38.2
dry from solution (0.0%)	152 ± 16.2
dry 0.5% HA	126 ± 33.7
dry 1.0% HA	90.9 ± 11.2
dry 5.0% HA	73.9 ± 8.70
dry 6.0% HA	92.5 ± 29.0
dry 10.0% HA	32.4 ± 22.5
dry 0.5% CaCl ₂	144 ± 10.7
dry 1.0% CaCl ₂	121 ± 44.4
dry 5.0% CaCl ₂	58.4 ± 30.8
dry 6.0% CaCl ₂	26.8 ± 14.6
conditioned 0.5% HA	110 ± 51.8
conditioned 1.0% HA	126 ± 46.3
conditioned 5.0% HA	74.0 ± 21.3
conditioned 6.0% HA	73.0 ± 18.6
conditioned 10.0% HA	77.9 ± 23.8
conditioned 0.5% CaCl ₂	109 ± 57.8
conditioned 1.0% CaCl ₂	136 ± 50.3
conditioned 5.0% CaCl ₂	122 ± 33.2
conditioned 6.0% CaCl ₂	104 ± 29.3

The CaCl_2 blends displayed a similar trend with increasing salt content. The “embrittlement” of the matrix by the incorporated salts is an effect in agreement with the notion that toughness is increased with an increased strain by the sliding of molecular chains. The incorporation of water into the polyamide did seem to increase the impact strength, especially at higher concentrations of filler. It possibly offset the chain hindrance induced by the filler particles, or salt ions.

Polarized Light Microscopy

Light microscopy studies gained insight as to the morphological changes induced on the material due to the incorporation of the salts. The changes observed, however, were actually more drastic between both sets of pure materials, those from pellets and those subjected to the acetic acid solution. Morphological changes were difficult to see between salt blends as the crystalline structure was so finely detailed that spherulitic growth was impossible to observe. As examples, Figures 65 and 66 contain micrographs from as-received polyamide pellets and material taken from solution.

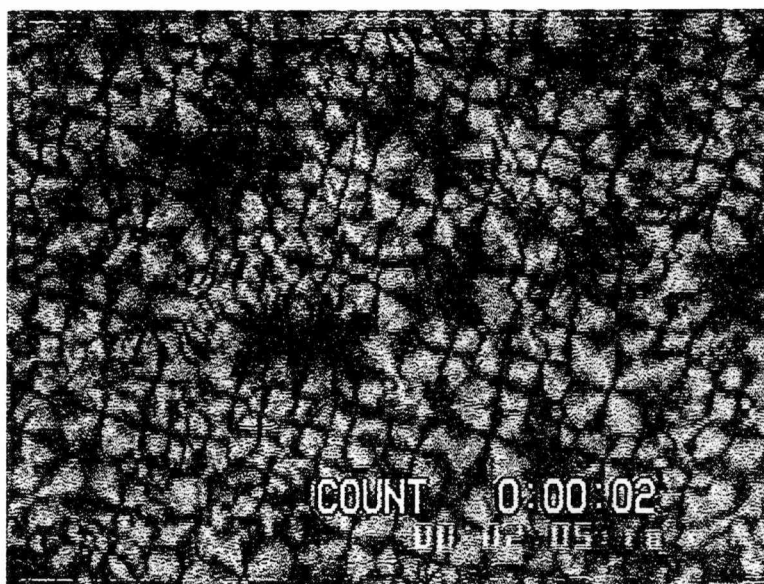


Figure 65. Polarized photomicrograph of as-received nylon 6. (~200x)



Figure 66. Polarized photomicrograph of solution treated nylon 6. (~200x)

CHAPTER IV

DISCUSSION

Thermal/Morphological Characterization

Differential Scanning Calorimetry

Characterization of the polymer blends using differential scanning calorimetry provides insight into the crystalline morphology of the polymer. The results for all blends, which were summarized in Table 9, show significant changes between as-received pellets and solution treated polymer.

The endothermic and exothermic changes are important to quantify as modification by acetic acid can severely degrade the polymer chains. In fact, this is one possibility for the reduction in melting temperature between these materials. In addition to the effect of residual solvent in the material not being driven off, small molecular chains may contribute to the plasticizing effect. The drop of melting temperature by 12°C as well as an increase in crystallization temperature would suggest the existence of a nucleating agent of some nature. A decrease in melting temperature would indicate that the molecular chains are more readily melted due to a shorter overall average in molecular length. They would not require as much energy to remove them from the crystal structure which results in the lower temperature observed. The smaller length chains could also be cause a reduction in the spherulite size in the solution treated samples. This reduction in crystallite size

would allow higher amounts of crystallinity and hence, result in an increase in the ΔH_m of the material.

It is known that low molecular weight samples of polymer chain can act as plasticizing agents and possibly nucleation sites for larger chains. Therefore it follows that the undercooling for a material with such constituents would be less than one without. This is observed between the as-received and solution prepared samples as an increase in the crystallization temperature of the materials. Given the same cooling rate, a polymer with a plasticizing agent, as well as smaller molecular chain segments to nucleate on, would crystallize faster, but possibly forming smaller crystal domains. Polarized light microscopy discussed in the next section provides evidence for these smaller crystalline domains as a result of the solution treatment

The presence of multiple melting peaks present in all of the blends is indicative of the reorganization of the polymer chains.[78](Jaffe) The multiple phases present in nylon 6 are distinguished by their order between and along the molecular chains. As the polymer is heated, a chain which is not ordered enough to fit into, say the α -monoclinic phase, would find sufficient energy to enter the crystal and then later be melted along with the rest of the prior-existing domain. Determining the contribution of particular chains, or phases to each melting peak would be an extremely difficult task, or one left to theoretical thermodynamics. The only assumption that can be made regarding this is that one would expect the higher order phases to melt at a higher temperature.

As noted earlier in Table 9, the hydroxyapatite blends showed virtually no change in the thermogram curves. This is due to little interaction between the matrix and filler materials. This, however, is not the case for the CaCl_2 blends

where a noticeable decrease in melting and crystallization temperatures is found. These changes are indicative of molecular interactions between the salt and the matrix. The effects due to increasing CaCl_2 salt content are shown by the thermograms for the 5.0% and 6.0% CaCl_2 blends in Figures 40 and 41. The positively charged salt ions are disassociated and prevent hydrogen bonding between the polyamide chains. The evidence for the destruction in hydrogen bonding was supported by spectroscopic findings using the FT-IR. Continued discussion of this carbonyl binding is presented later. Although known to effect the amorphous chains in this manner, it is a significant observation that it hinders the ability to form even lower ordered crystalline phases.[54](Valenti) This binding action forces the chains apart and into a possible type of smectic, or nematic arrangement with limited long range order.

The melting point depression presented in Figure 42 is described in terms of this free energy of binding by Flory. The free energy of binding is thermodynamically presented as

$$\Delta G_u = -pRT \ln(1 + Ka_s) \quad (27)$$

with K being the binding constant between the salt and the amorphous polymer, a_s the salt activity, and p the number of binding sites.[73] (Flory) The equation helps quantify the extent by which the salt ions have interacted with the molecular chains. Due to lower amounts of crystalline order in the polymer, the energy required to move the molecular chains into a disordered state is lowered significantly. The disordered state is expressed as an entropy of fusion, or ΔS_u . The entropy of fusion is a key factor in affecting the melting temperature and correlates to the melting state conformation of the chains.[79](Mandelkern) The free energy,

therefore, can be related to the heat enthalpy, ΔH_u of the idealized crystalline melting peak through the equation

$$\Delta G_u = \Delta S_u (T_m^o - T) \quad (28)$$

and Equation 21. An example of the significance of the entropy of fusion resides in the values of enthalpy for polyesters and polyamides. Despite the hydrogen bonding of polyamides, the enthalpies are virtually identical.[80](Mandelkern) This suggests that in this particular case the melting point depression is governed by changes in the entropy of fusion as well, but due to disruption by CaCl_2 salts.

Polarized Light Microscopy

The findings for PLM are complimentary to the above findings for DSC measurements. The crystallization changes between as-received pellets and solution prepared materials found in the DSC, namely melting and crystallization shifts, were observed visually. As shown previously in Figures 65 and 66, there is a significant morphological change. The original, as-received pellets contained spherulites with diameters of approximately 24 microns as seen under the light microscope. Solution treated samples produced smaller and more numerous crystalline areas hardly discernible by eye. No approximation as to the resulting dimensions can be made by this visual method. The same explanation for the shifts in crystallization temperatures can be applied here. The cleaved molecular chains due to the solution may be acting as nucleation sites for the larger molecular weight chains in addition to being plasticization elements. This results in more rapid crystallization of the polymer as well as significantly smaller "spherulite-like" structures, if they are indeed spherulitic in nature.

Lack of microscopic structures were observed only for the 5.0% and 6.0% CaCl_2 blends. As one would have expected from the DSC results the disassociated salt ions bound the molecular chains and did not allow crystallization to occur. The result was a translucent material in which little, or no interference was observed under crossed-polars.

Infrared Spectroscopy Analysis

Confirmation of the crystallinity results found using calorimetry was performed with the FT-IR. It is seen in Figures 48 and 49 that hydroxyapatite blends change only slightly and those of the CaCl_2 blends change dramatically. Changes in the quantitative amounts of the various crystalline phases has been performed by a number of groups, however, it requires extensive calibration of the technique. For instance, 1124 cm^{-1} corresponds to the amorphous regions, 1170 cm^{-1} to the amorphous and pseudo-hexagonal γ phase, and 1199 cm^{-1} to the α -monoclinic phase. The ratio of these peaks with the appropriate calibration factors can determine exact fractions of the various phases.[81](Simak) The crystalline bands in this case were used mainly as a qualitative measure of crystalline fraction.

The C-CO stretch absorbance band is indicative of the relative degree of motion allowed for the carbonyl. It is clear that with a crystallinity of 35%, there exists free vibration of C=O to add to this stretching. In the case of the hydroxyapatite blends these crystalline sensitive peaks are still evident. With the addition of 5.0% Ca^{++} ions this free C=O is effectively bound, resulting in lower energy available for the C-CO stretching. This can also be seen if one looks at the

differentiation spectra of the blends in Figures 50 and 51. There exists a clear decrease in the absorbance of the "free" carbonyl peak.

Wide Angle X-ray Considerations

As with the other crystallinity determining experiments, x-ray analysis clearly indicates the effects of CaCl_2 on the polyamide matrix. Because of the attraction of the Ca^{++} ions the reflection planes for any crystalline phases are no longer in alignment and hence, display no significant intensity.

Crystalline order in the polyamide matrix can also be quantified by comparing the relative amounts of the pseudo-hexagonal γ and α -monoclinic phases. Knowing now that hydroxyapatite has little effect on the crystallinity it is possible to observe the effect of moisture. Comparing the conditioned blends of hydroxyapatite to those of the dry indicates a slight increase in the more ordered α -monoclinic phase. This suggests that it is possible water actually allows the molecular chains to move slightly and form a more ordered structure. Additionally, the addition of moisture appears to lower the overall scan intensity with increasing hydroxyapatite content without modifying the relative amounts of crystalline and amorphous area. Therefore, one would conclude that water has a "global" effect on all angles of x-ray diffraction, changing the material's overall ability to absorb the x-ray radiation. Exactly what morphological changes are taking place to cause this decrease in diffraction intensity is unknown.

Dynamic Mechanical Contributions

Although minimal chemical interactions are taking place between the hydroxyapatite filler and the polyamide there exists a certain amount of physical chain hindrance. This is shown as an increase in the $\tan \delta$ transition temperature. The effective increase in this transition indicates that the filler is binding the amorphous regions of the polymer and creating a need for additional energy to allow them to move. This effect decreases in the 10.0% hydroxyapatite sample and is due to agglomeration of the filler material. Instead of being evenly distributed throughout the matrix, the particles are attracted to themselves and lower the surface area that is exposed to the randomly coiled chains.

The most intriguing data is that acquired for CaCl_2 blends. The $\tan \delta$ curves in figures 56 and 57 show additional transitions not seen with the hydroxyapatite blends. Focusing primarily on the dry samples one notices a secondary relaxation above the normal T_g . This secondary relaxation is an effect of the Ca^{++} ions binding with the amorphous chains. Evidence for this was provided via the earlier methods of characterization and can explain the high temperature required for this transition. Because the $\tan \delta$ is a measure of the relative mobility of the amorphous phase, this transition must be a highly hindered section of amorphous content.

The introduction of moisture into the polyamide has noticeable consequences on the T_g of the material. Because water acts as a plasticizer it broadens the loss peak owing to the fact the water continues to "lubricate" the material until it is transformed to vapor and driven off. As well, the transition's intensity increases relative to the other peaks, even compared to the secondary transition found in the 5.0% and 6.0% CaCl_2 blends.

As noted earlier the hydroxyapatite blends do not change significantly in regards to the storage modulus, hence the focus is on that of the CaCl_2 blends and specifically the 5.0% and 6.0% compositions. The incorporation of the salt ions into the matrix brings with it a reinforcement of the matrix up until the point where this secondary bonding between ion and carbonyl is thermally terminated. Interestingly enough the storage modulus experiences a curious drop in magnitude just before the secondary reinforcement takes place. The mechanism taking place at this point may be centered around the lower amount of crystallinity evident in the samples. Without this stability incorporated by the crystalline phase, the polymer would effectively melt prematurely being completely amorphous. However, the existence of the ion-bound amorphous phase imparts "last-minute" stability into the material before the final melting occurs.

Tensile and Impact Properties

The objective of the above characterization techniques was to impart some understanding into the overall mechanisms of deformation observed through the tensile and impact tests. The insight provided by the previously described techniques helps to elucidate the relationship between the morphological changes of the blends and their respective contributions to the macroscopic properties.

The modulus and tensile stresses for the injection molded dry and conditioned hydroxyapatite blends could be found using the theories from Sato-Furukawa for modulus and Kerner for tensile stresses. The premise behind the use of the Sato-Furukawa model hold substantially based upon the spectroscopic characterizations. These techniques found little, or no interaction between the filler

and matrix and this applies directly to the assumption that the filler particles provided no reinforcement for the matrix assuming no adhesion between them. The result is a fairly accurate description of the experimental findings (Figures 17 and 20). As with the modulus predictions the tensile prediction provided by Kerner also followed this same assumption of no adhesion between filler and matrix. Owing to the fact that the filler will not contribute to holding the load, the tensile stress effectively drops.

A more drastic result of no adhesion between the matrix and particulates is that for the strain to break. The filler in this case becomes a void, which in terms of crack growth forms a perfectly suitable initiation point. The maximum strain suffers because of this and a reduction of 85% occurs no matter the concentration of filler.

Due to the particular nature of the CaCl_2 blends their mechanical properties were not easily predicted. There is no theoretical basis to determine the enhancement of properties with the addition of CaCl_2 due to the fact that CaCl_2 disassociates as well as interacts chemically with the polymer chains. Thermodynamic parameters have been calculated based upon interactions between the molecules, however, these are not readily translated into macroscopic details. Hence, the tensile results for the CaCl_2 materials do not follow predictable patterns.

An explanation of the effect of incorporating the CaCl_2 salts can be presented despite the difficulty in predicting their behavior. The reduction in modulus for the injection molded samples, as seen for the hydroxyapatite blends can be explained in terms of crystalline contributions. The bonding strength between the Ca^{++} ion and the carbonyl is slightly lower than that of the hydrogen bonding associated with the crystalline structure.[82](CRC) Therefore, increasing the

amount of salt content reduces the material's effective crystalline contribution enough so that the modulus, which depends heavily upon the crystalline portion for elasticity, is reduced.

If the calcium ions are incorporated into the amorphous portion of the polyamide, it therefore stands to reason that increased bonding energy is provided by the calcium ions between molecular chains. This would result in an increase in the tensile properties due to the increased chain hindrance. This would also contribute to a loss in plasticity, resulting in a drop in strain to break. These ideas on molecular chain effects are exactly as observed. The difficulty in the predictions, however, is the effective saturation point found for this particular system. Between 1% and 5% salt content there is a downward turn in the reinforcing trend. At this point there exists a significant amount of ions to successfully bind the chains that would normally form crystalline phases. This drastically alters the nature of the polymer's response to an applied load and the mechanical properties are seen to decay. The structural element, the crystalline phase, is being destroyed and along with it the material's load carrying ability.

Similar consequences due to the introduction of filler are seen in the impact results as are the tensile properties (Figure 64). Because this test is essentially an induced tension loading at high strain rates it is possible to apply similar morphological theories. The Kerner predictions have performed this exact manipulation and merely calculated a modulus term and placed it into an equation for calculating impact energy (Eq. 24). Naturally this prediction follows similar trends as that for the reduced tensile stresses. The prediction, however, does not strictly hold even in regards to the hydroxyapatite blends. The combined effect of the filler being a crack initiation site as well as the increase in strain rate results in

a significant reduction in properties. The only compensatory effects come from the incorporation of water, which helps to plasticize the matrix and bring it closer to the predicted values. This is seen as a slight increase in relative impact strength at the higher concentrations of filler. Otherwise, impact strength has been reduced, in a manner similar to that of the strain to break, approximately 80%.

Distinction as Bone Analogues

To compare these materials to that of human bone one must specify what part, or parts of bone are to use. As discussed earlier, the modulus and tensile properties of bone can vary tremendously depending on what part of the body it is removed from as well as whether it is sectioned from the compact bone, the cancellous region, or the trabecular region. Each of these specific bone types have a set of characteristic properties well suited for it's function. Additionally, moisture content plays a significant role in the material's energy absorption abilities. Hence, to make effective comparisons between the bones and the analogues the values reported in this section are for conditioned, or wet samples.

Another significant factor to consider when comparing the mechanical properties is the method by which they were attained. Currently there are no standard testing procedures for sectioning bone samples, applying loads, etc. Therefore, one must be willing to accept that most of the reported property values for bones reflect a characteristic set of preparation and loading procedures. An example of this is the testing procedures for impact studies. The majority of the published energy absorbing values are integration of stress-strain curves performed at a high rate of strain. True impact studies have not been performed on

standardized impact specimens, such as Izod, or Charpy as is the case for polymers, metals, or ceramics. The true impact studies that have been performed have specific loading conditions and specimen dimensions, typically an entire femur, tibia, or bone of interest. Therefore, the comparison of all impact studies will result in a broad spectrum of reported energy values. Despite the shortcomings of standardization however, comparisons to similar testing conditions performed for this research will be used to quantify the experimental data in relation to recently published bone properties.

Evans and Lebow sectioned 242 samples of compact bone from 12 femurs in an attempt to determine regional variations in properties.[9] If one compares the polyamide experimental data from this work to properties of the compact bone removed from the femur, significant differences are found. Table 15 shows these comparisons. Most notably is the decade of difference between the magnitudes of

Table 15. Nylon 6 analogue mechanical properties vs. compact bone.

Mechanical Property	Compact Bone (Range)	Polyamide Analogues (Range)
Elastic Modulus, E [6](Carter)	17.5 GPa (15.6-19.4)	1.4 GPa (1.17-1.52)
Ultimate Tensile strength, σ [9](Evans)	113 MPa (88-167)	59.7 MPa (34-84)
Strain to Break, ϵ [6](Carter)	1.75% (1.3-2.91)	15.3% (3.5-45)
Energy Absorption (in.-lb./in ³)[77](McElhaney)	260	108 (73-136)

the elastic moduli. As a modeling material for compact bone, these particular polyamides clearly require some improvement in the elastic modulus. A solution to this is the addition of glass fiber to the matrix akin to the polyamide studies

performed previously in our labs. The work and resulting changes in impact strength are noted in Reference 16.(Snider)

The properties of the polyamide analogues from the present study compare more favorably to the properties of trabecular and cancellous bone. Figure 67 shows a comparison between a typical stress-strain curve for cancellous and trabecular bone (sectioned from the tibia) with accompanying samples of polyamide/salt blends.[83][5](Keaveny)(Rohl) The hydroxyapatite samples fall directly between the two extremes of the different sections of bone. Additionally, the strain to break is similar for both cases and the ultimate tensile strength is virtually identical to trabecular values. Numerical comparisons between the cancellous bone, trabecular bone, and 10% hydroxyapatite are shown in Table 16.[83][5](Keaveny)(Rohl) The agreement of the 10% hydroxyapatite blend with the trabecular bone is quite promising, except for a slightly lower modulus in the blend.

Table 16. 10% HA blend properties vs. cancellous and trabecular bone.

Physical property	10% hydroxyapatite	Cancellous bone	Trabecular bone
Elastic modulus, E (GPa)	1.17 ± 0.169	0.48 ± 0.32	2.63 ± 0.73
Tensile strength, σ (MPa)	34.4 ± 3.95	2.54 ± 1.18	23.6 ± 8.28
Strain to break, ϵ	3.45 ± 0.58	1.55 ± 0.49	1.37 ± 0.33
Energy Absorption (in.-lb./in ³) (integrated)	56.5 ± 17.3	5.04 ± 2.55	61.8 ± 14.8

It may also be possible to enhance this property with the addition of glass fiber reinforcement. The downside to this approach, however, would be an increase in the tensile strength. The absorbed energy comparisons are not completely valid, as the tests were performed at different rates, 0.005 sec^{-1} on

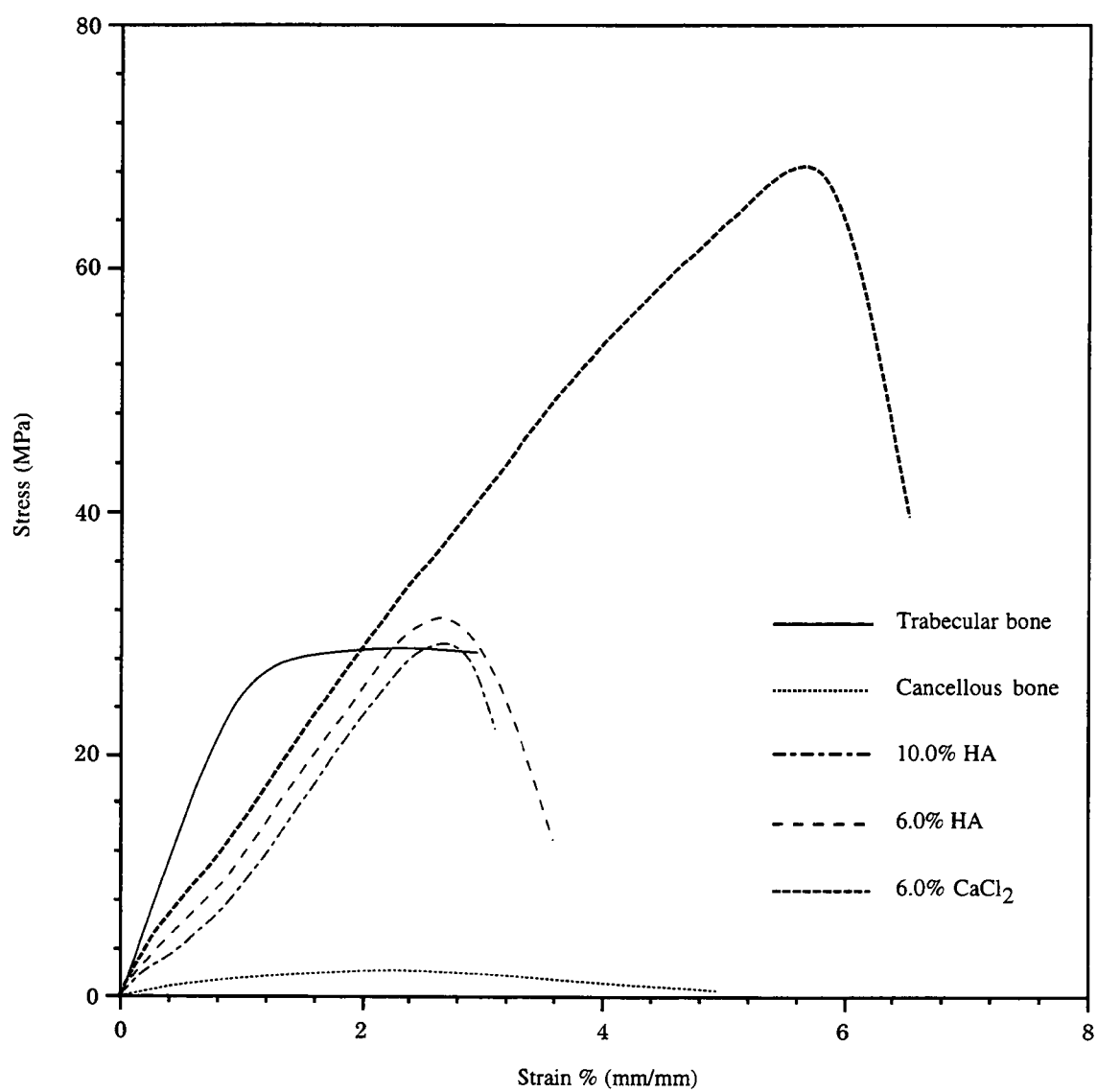


Figure 67. Stress-strain curve of bone and polyamide bone analogue.

trabecular bone and 0.02 sec^{-1} in this research. However, the energy values obtained in the present research from the high strain-rate impact test of the hydroxyapatite samples agree fairly well with the integrated stress-strain method.

If one is to take a holistic approach to designing an appropriate analogue, the most influential parameter for consideration is shape. The published bone data presented here had variations in the testing shape, i.e. cylindrical and rectangular and correlation of these property values to actual bone dimensions has limitations. Stress risers due to geometry are a critical factor in the overall performance of either a bone, or an analogue. Therefore, it would be necessary to systematically section bone samples and polyamide materials in a similar manner, taking care to ensure that conditioning of the samples is also consistent.

Neglecting the effects of geometry for a moment for the sake of simplicity a proposed configuration for the next step in creating a whole bone analogue is presented in Figure 68. This model draws upon the various mechanical property variations found in this study and those of previous ones to satisfy the loading needs in a typical human long bone. The matrix material consists of nylon 6, but depending upon the region of interest, glass-fiber and salt content are varied to accommodate the variation in real bone. For instance, the mechanical properties desirable in compact bone, high impact strength, a tensile strength of $\sim 150 \text{ MPa}$, and strain to break of 1.0% are fulfilled by the use of glass fiber-reinforced nylon 6. The areas of trabecular bone would be modeled with a conditioned 10% HA blend to mimic the desired properties.

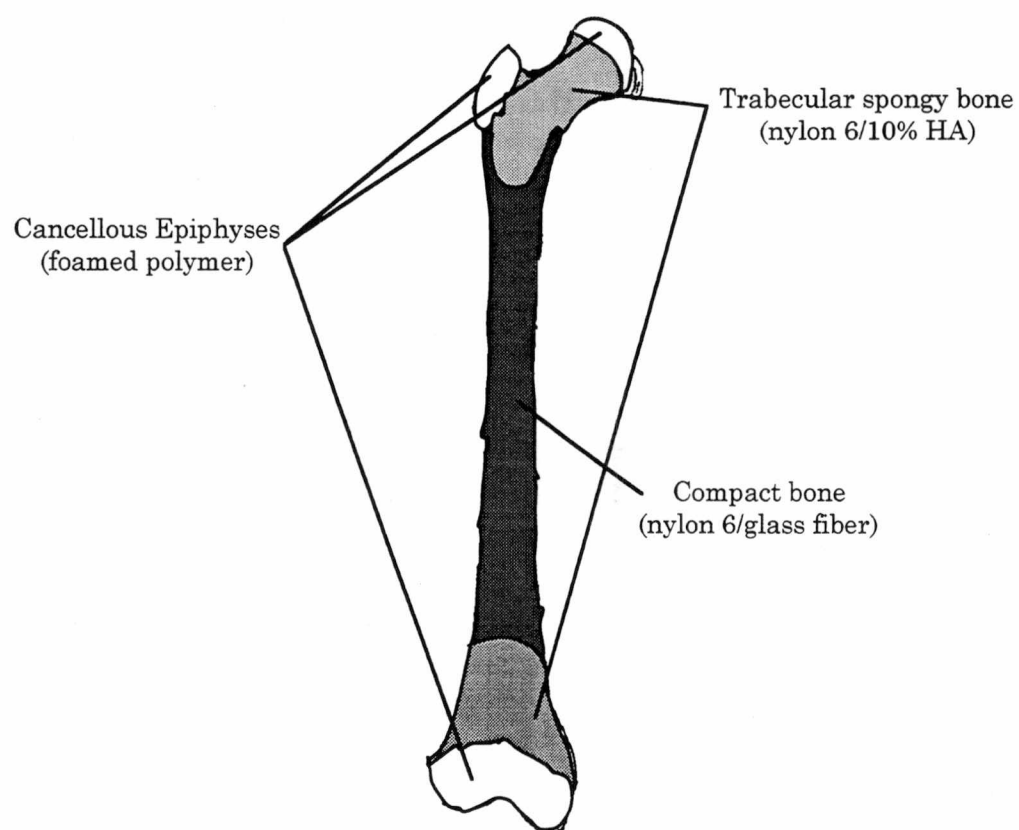


Figure 68. Structural composition of proposed polyamide analogue.

CHAPTER V

CONCLUSIONS & RECOMMENDATIONS

This study clearly shows the variability with which a polymer matrix can be modified using a particulate filler. The demonstration that an engineered polymer system can closely model that of a bone in material properties was confirmed. Values of strain to break and tensile stress were modified such that they agree favorably with those published for trabecular bone in the human tibia.

An additional area of interest that has been demonstrated by the presented material is the effect of CaCl_2 salts on the morphology of the polyamide matrix. Specifically, a proper theory for determining the changes in tensile properties is needed that accounts for the molecular interactions of the disassociated ions with the polymer. The simplistic filler models described here do not predict these properties because it requires an additional thermodynamic assessment of the interactions. Hence, the following suggestions should be considered as further work in these areas:

1. Investigate the effect of geometry on the impact resistance of the analogue.
2. Process a complete analogue that incorporates the glass fiber and salt system into one injection molded bone analogue.
3. Develop an appropriate theory for determining the mechanical property changes with the incorporation of CaCl_2 and similar salts.

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VITAE

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