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Reactive processing and material characterization of thermoplastic and thermoset polymers and their composites

Ning, Xin, Ph.D.
Case Western Reserve University, 1991

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REACTIVE PROCESSING AND MATERIAL CHARACTERIZATION
OF THERMOPLASTIC AND THERMOSET POLYMERS
AND THEIR COMPOSITES

XIN NING

submitted in partial fulfillment of the requirements
for the Degree of Doctor of Philosophy

Thesis advisor: Professor Hatsuo Ishida

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May, 1991
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ABSTRACT

by

XIN NING

The characteristics in the understanding of reactive processing are examined in the studies of two research projects, one involves the synthesis and material characterization of a thermoset phenolic material while the other involves RIM-Pultrusion processing of fiber reinforced composites of thermoplastic nylon-6 and rubber-toughened nylon-6.

A series of compounds with difunctional benzoxazine groups was synthesized. They form structures characteristic of phenolic material through a self initiated ring-opening reaction mechanism that releases no condensation byproduct during the curing reactions. This family of compounds offers greater flexibility than conventional novolac or resole resins in terms of molecular design. It was demonstrated that by design of the molecular architecture of the benzoxazines from different primary amine and bipheno1 structures, materials with mechanical properties superior to conventional phenolic material and ease of processing could be obtained. The dynamic mechanical properties of the phenolic materials were studied by mechanical spectroscopy. The γ relaxation in the phenolic materials was
related to the structure of the substituent groups attached to the nitrogen atoms in the crosslinked networks.

In the curing of two benzoxazine precursors into phenolic materials, the reaction kinetics and structural evolution were monitored by dynamic mechanical experiments at below the ultimate glass transition temperatures of the materials. The structures of the polymerizing mass were probed by stress relaxation experiments. It was found that the gelation behavior of the precursor based on bisphenol-A and methylamine could be adequately detected by the dynamic moduli measurement of the curing material. However, the precursor based on bisphenol-A and aniline exhibited, prior to the macroscopic gel formation, in the stress relaxation experiments a feature of two sets of relaxation processes that resembled in the time domain the transition and terminal zone relaxation behaviors of a thermoplastic material. The pseudo-gel structures detected by dynamic experiments were probably due to physical interactions and topological frictions among highly branched chains which were intermediates in the formation of crosslinked networks. In this case, the dynamic experiment could not be used to determine the true chemical gel point.

RIM-Pultrusion process was successfully applied to prepare unidirectionally reinforced composites of nylon-6 and rubber toughened nylon-6. The composites exhibited excellent wetting and mechanical integrity due to the low viscosity of the precursors used in the process. The possibility of engineering the composite impact failure behaviors by using rubber toughened matrices was demonstrated.

The $\beta$ relaxation process was shown to occur at different temperatures and exhibit a different activation energy for dry and wet samples which were prepared by reaction injection molding (RIM) of nylon-6. By employing a low operating
frequency and controlled low moisture levels, it became possible to distinguish the two $\beta$ relaxation processes, $\beta_1$ and $\beta_2$, in one sample by dynamic mechanical spectroscopy. It was shown that while $\beta_1$ was associated with moisture in the sample, $\beta_2$ was related to a structural mechanism independent of moisture. The effect of moisture content on the chain-chain association ($\alpha$ relaxation process) and chain-water association ($\beta_1$ relaxation process) in nylon-6 was assessed. The annealing mechanism of RIM nylon-6 at 85°C was probed by both dynamic mechanical spectroscopy and X-ray diffraction.
DEDICATION

... to my family, especially to my mother, for the suffering and sacrifice it had endured, for the love and support it provides, and for the future.

... to my wife for her continued love and encouragement.
ACKNOWLEDGMENT

The author would like to express his sincere thanks and appreciation to professor Hatsuo Ishida for his guidance and support throughout the researches. The author especially appreciates the atmosphere of freedom and openness in research and the pursuit of scientific innovative thinking.

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Chapter I

INTRODUCTION
Polymer processing is an activity of converting raw materials into finished polymeric products of desirable shapes and properties. If chemical reactions are encountered during the shaping or forming processes, they are called "reactive processing". Reactive processing exists in a wide range of applications of polymeric materials. For thermoplastic materials, there are reactive extrusion, reactive compounding, and reaction injection molding, etc. The forming processes of thermoset materials, in a broader understanding and definition, all belong to the reactive processing category since the precursors (or resins, which have relatively low molecular weight and finite structures) of thermoset materials are transformed into macroscopic crosslinked structures during processing.

It is appropriate for us, in this introduction section, to examine the features in reactive processing, to illustrate the principles governing the study of reactive processing and the techniques used therein, and to apply these principles in guiding the research activities.

The Need for Reactive Processing

It may be summerized as economy and necessity. In majority of the reactive processing of thermoplastic materials, it is economically advantageous to perform some of the chemical modifications on the base polymer systems during processing. For multi-component systems as polymer blends and filled composites, chemical modifications during the processing will influence strongly the morphology and physical performance of the final materials. It also offers the versatility of custom-tailoring the performance of the final products. Reaction injection molding (RIM) of thermoplastic polyurethanes and nylon-6 is a necessity due to the fast kinetic nature of the reactions as well as economic considerations.
The low viscosity of the reactive precursors makes it possible to mold large parts or parts with intricate shapes with low mold filling pressure and small clamping force. Reactive processing further eliminates steps to produce, purify, and sometimes pelletize polymers prior to the shaping process, since it directly uses polymer precursors as raw ingredients. For thermosetting materials, it is then absolutely a necessity because there is no other way to achieve the same objective. In the field of high performance composite materials, a majority of the current applications are based on thermoset matrices while in recent years thermoplastic matrices are attracting great attention. With the increasing use of fiber reinforced polymeric composites in structural applications, the scientific understanding of the sophisticated chemical, physical changes in the polymeric matrices and in the polymer-fiber interfaces during the reactive processing becomes more demanding. The characteristic in reactive processing distinguishes itself from conventional polymer synthesis and plastic processing.

Multi-discipline Nature in Reactive Processing

Reactive processing is multi-discipline by its nature. Its subject represents, in the author's view, a fusion of science and engineering. The methodology of study involves synthetic chemistry, physical chemistry or particularly structure-property relationships, and of course the manufacture process engineering. The commingling of the disciplines adds new dimension to and sets certain restrictions on each one of them. Thus we need creative design of synthetic chemistry to adapt the chemical reactions to certain process requirements; we need to understand the physical chemistry of structural and morphological development during the chemical reactions; we need to understand how the chemical reactions influence
processing parameters and vice versa; furthermore we need to design new manufacturing processes for certain chemical systems to achieve best performance.

Characterization Techniques for Reactive Processing

As is mentioned in the section above, the study of the chemistry and physical chemistry during the process plays a major role in understanding and utilizing reactive processing. Serving this objective are a series of characterization techniques to analyze and correlate structures and properties, from molecular level to macroscopic level, of the reaction systems.

Molecular characterizations of both the starting and the resulting materials are essential in understanding the molecular basis of the physical changes. The molecular spectroscopic techniques such as nuclear magnetic resonance (NMR), infrared spectroscopy (IR), and ultraviolet spectroscopy (UV) are widely used. In modern instrumentation, Fourier transform (FT) operation greatly enhances the sensitivity and efficiency of the analytical instruments. As important are the chromatographic techniques which separate material components before analysis can be carried out. Of the great variety of gas phase (GC) and liquid-liquid, liquid-solid phase (LC) chromatographic techniques, gel permeation chromatography (GPC) which separates components by their hydrodynamic sizes is more widely used in polymeric analysis to obtain molecular weight and distribution of the material systems. Another part of the molecular characterization is the analysis of the process, during which the molecular changes occur, or the kinetics of the reactions. Essentially all the analytical techniques could be used for such purposes with consideration of the time variable. However, techniques with very fast acquisition capability have a definite advantage, especially in analyzing fast reaction
processes such as RIM. FTIR is one of the techniques with such capability and has been applied extensively in kinetic studies of chemical reactions and physical transformation (crystallization, for example).

On the other end and equally important are the study of the macroscopic structures and properties of the polymeric materials. X-ray diffraction is a classic tool in studying the structure of crystalline and semi-crystalline materials. Thermal analysis (differential scanning calorimetry (DSC)) is one of the techniques) provides information about the thermal response accompanying a reaction or a physical transformation. Microscopic techniques such as optical microscopy (OP) and electronic microscopy (scanning or transmission electron microscopes (SEM or TEM)) are powerful tools in studying the morphological features and organizations in the materials.

Property evaluation of the materials serves the ultimate purpose of material research and development effort. Mechanical properties of polymeric materials and their composites are the prime properties for structural applications in which the material stiffness (modulus), strength, and damage tolerance (fracture toughness) are of prime importance. Other specific bulk properties, such as dielectric, heat-resistant, and functional responses (optic, electro-optic, bio-compatibility, etc.) are important for certain applications of polymeric materials and the corresponding evaluations should be carried out accordingly.

The understanding of the relationships between molecular structures and macroscopic properties is the basis for molecular design of materials. By combining molecular and bulk characterizations, one would be able to draw structure-property relationships. This is especially important for optimizing reactive processing since both molecular and bulk structures change during a single process.
One characteristic behavior of polymeric materials is the pronounced material viscoelasticity which distinguishes themselves from conventional metallic or ceramic materials. Study of material viscoelasticity is also able to provide the bridge between molecular motions and macroscopic properties. If we perturb the system mechanically, the resulting viscoelastic response of a solid material as a function of temperature (or frequency, or both) is called a mechanical spectrum and the method mechanical spectroscopy. The viscoelasticity of fluid systems such as polymer melt or reactive precursors is observed in their flow characteristics by a rheometer. During reactive processing, the change of viscoelasticity as a result of chemical reactions will be measured in their rheological properties. On the other hand, the changing rheological behavior reflects the change in molecular architecture in the reacting systems. Thus rheological understanding of the system is indispensable for reactive processing since it provides not only detailed information for process engineering design but also scientific understanding of the reaction systems.

Scope of the Current Research

The thesis is consisted of two research projects. The first is the development of a new approach towards the preparation of thermoset phenolic materials which exhibit structural, performance, and process advantages over traditional phenolic materials. The second is the processing and material characterization of thermoplastic nylon-6 and rubber toughened nylon-6 polymers and composites produced from RIM and RIM-Pultrusion processes. In each of the projects, quite diversified subjects have been studied. These include chemical synthesis of the precursors, molecular characterization of the compositions and structures,
mechanical and dynamic mechanical properties of the materials. Rheology and chemorheology of the reaction systems, reactive processing of polymers and composites, morphology of the composites, dynamic mechanical analysis of the molecular relaxation processes in the solid state. It is the author’s belief that the diversification of the research activities reflects the characteristics encountered in reactive processing and that all the techniques used in both thermoplastic and thermoset materials serve under the general philosophy governing the study of reactive processing.

Thus, the first part of the thesis consists of three chapters (Chapters II, III, IV), dealing with several aspects of the new phenolic materials: synthesis and characterization, structure-property relationships, and chemorheology individually in each chapter. The second part consists of two chapters (Chapters V, VI) with Chapter V on the processing and properties of nylon-6 and rubber toughened nylon-6 composites. Chapter VI focuses on the fundamental dynamic relaxation behavior of pure RIM nylon-6 which serves as the basis for understanding of the more complex dynamic mechanical spectra of the nylon composites encountered in Chapter V.
PART 1

PHENOLIC MATERIALS

VIA RING-OPENING POLYMERIZATION
Chapter II

SYNTHESIS AND CHARACTERIZATION OF BISPHEROL-A BASED BENZOXAZINES AND THEIR POLYMERS
INTRODUCTION

Traditional phenolic materials are the crosslinked products of their low molecular weight precursors, either of novolac or resole type. These approaches have been successful in bringing about the first class of synthetic plastic materials since the turn of the century. The materials obtained exhibit good heat-resistant, flame-retardant, and dielectric properties. Thus, they have been widely used in construction, household, and electrical facilities. Another notable advantage is that the raw materials and the fabricating process are very inexpensive. A recent book on phenolic materials has given thorough overview to this well established discipline (1). However, there are a number of shortcomings associated with these traditional phenolic resins, namely the brittleness of the materials, release of water and ammonia during the curing processes due to condensation reactions, use of strong acids as catalysts, and poor shelf life. The use of phenol and the process to synthesize novolac or resole precursors in aqueous medium create significant threats to environment as well as to human health. Thus, the revitalization of phenolic materials for high performance composite and electronic applications depends, to a large extent, on our ability to create new chemistry and processes to overcome the aforementioned shortcomings.

3,4-dihydro-3-substituted-1,3-benzoazazines (abbreviated as benzoazazines hereafter) are heterocyclic compounds synthesized by reaction of the corresponding phenols, primary amines, and formaldehyde. They were discovered as Mannich reaction products from these reactants (2,3). A patent was issued for their synthesis and use as surfactants (4). Later, benzoazazines were found to react almost specifically with the ortho position of a phenol compound to form a dimer with methylene-amine-methylene bridge structure (5,6). Benzoazaine structures
were also found by nuclear magnetic resonance (NMR) spectroscopy as intermediates in the curing of novolac resins (7). In the meantime, heating of benzoxazine compounds into a hard, brittle mass was patented without specifying the structures and characteristics of the products (8,9). Recently, Riess et. al. studied the reactions of mono-functional benzoxazines with phenol initiator in the bulk by NMR and gel permeation chromatography (GPC). They showed that only oligomeric phenolic structures with average molecular weight around 1000 were obtained. No materials could be made from this approach since the theroxidissociation of the monomer competed with the chain propagation reaction so that high molecular weight linear structures were unobtainable (10). The use of compositions consisting of both polyfunctional benzoxazines and reactive polyamines for coating and encapsulating was documented in the patent literature recently. The reaction involved opening the benzoxazine rings with a primary or secondary amine (11,12). As the first step towards developing a new class of phenolic materials, this chapter presents the synthesis and characterizations of phenolic resin precursors through the use of difunctional or multifunctional benzoxazine compounds, and their curing into phenolic materials with the ring opening reaction being initiated by the dimers and higher oligomers in the resin composition.

EXPERIMENTAL

Benzoxazine based on bisphenol-A and methylamine was synthesized according to the following scheme:
The bisphenol-A was supplied by the Shell Chemical Company. Other chemicals and reagents were purchased either from the Aldrich or Fluka companies. All chemicals were used without further purification.

The composition of the reaction product is influenced by the choice of reaction medium. A general procedure is as follows: To the mixture of 0.4 mole formaldehyde aqueous solution and 80 ml dioxane in a 500 ml three neck flask equipped with thermometer, condenser, dropping funnel and cooled by ice bath, 0.2 mole methylamine in 20 ml dioxane was slowly dropped in, keeping the temperature below 10°C. The mixture was stirred magnetically for 10 minutes before adding in the solution of 0.1 mole bisphenol-A in 100 ml dioxane. The temperature was then raised, and the mixture was allowed to reflux for six hours to obtain a transparent solution. The solvent was then evaporated by a rotovap, and the viscous fluid was dissolved in 200 ml ethyl ether. The ether solution was washed several times with water to eliminate any unreacted formaldehyde or methylamine and dried over sodium sulfate. Evaporating the ether resulted in a viscous fluid at room temperature. The name of the precursor thus obtained will be abbreviated as B-m throughout the thesis as a reference to its original ingredients: bisphenol-A and methylamine. Only formaldehyde is the common ingredient of all the benzoazines studied. The composition and structures of the precursor were analyzed by proton nuclear magnetic resonance (NMR) spectroscopy in CD₃Cl as
well as gel permeation chromatography (GPC) and Fourier transform infrared spectroscopy (FTIR).

The NMR spectrometer used was a Varian XL-200 instrument operating at 200 MHz. The GPC was performed on a Waters instrument equipped with three styrogel columns of molecular weight range from 200 to 200,000, with a 254 nm fixed wavelength ultraviolet (UV) detector and a refractive index (RI) detector. The equipment was controlled and data acquired under the Waters Maxima 820 workstation system. HPLC grade tetrahydrofuran (THF) was used as the solvent. The FTIR spectrometer was a Bomem Michelson 110 equipped with a high sensitivity liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector with a frequency range of 5000 to 500 cm\(^{-1}\) and operating at a fixed resolution of 4 cm\(^{-1}\). A Perkin Elmer-7 differential scanning calorimeter (DSC) instrument was used to examine the thermal characteristics of the curing process. The material transitions and relaxation properties were studied with a Rheometrics RMS-800 dynamic mechanical spectrometer (DMS) with torsional deformation applied to rectangular samples cured at certain conditions. The operation frequency was 1 Hz at a typical strain of 0.08%.

RESULTS AND DISCUSSIONS
Composition and Structures of the Precursor

The Mannich reaction illustrated above was found to represent almost complete conversion of the starting bisphenol-A to its benzoxazine and derivatives. The GPC chromatograph (from UV detector) of the benzoxazine composition is presented in Figure 1 along with that of bisphenol-A. The strongest peak at retention time 30.5 minute is assigned to the difunctional benzoxazine monomer.
The peaks with shorter retention times represent dimers and higher oligomers whose structures will be explored further in the following section. The bisphenol-A peak actually appears at a retention time of 29.7 minutes, shorter than its benzoxazine counterpart although its molecular weight is smaller. This phenomenon reflects the effect of molecular structures on the hydrodynamic volume of each compound. Thus, the existence of hydroxyl groups in bisphenol-A makes the molecule to take a larger hydrodynamic volume than that of the bifunctional benzoxazine of bisphenol-A at the THF environment in the GPC column.

The proton NMR spectrum of the B-m benzoxazine precursor along with the assignment for each resonance are shown in Figure 2. However, the percentage of each individual component is difficult to determine since the detailed structures of the dimers and higher oligomers are not known. Listed below are some of the possible structures for the dimers of bisphenol-A benzoxazines
Because the number of possible structures in dimers and higher oligomers is so large, not to mention the possible existence of branched and cyclic structures, it would be very difficult to determine the composition of each and every component in the product by \( ^1H \)-NMR alone. However, it is possible to determine the ratio between the number of methylene units in the benzoxazine ring (Figure 2, e and d with chemical shifts at 3.90 and 4.75 ppm) and the number of the methylene units existing in the bridge structures (f with chemical shift 3.68 ppm) by examining their integrated intensities of the resonance peaks. It is 4:1 for this synthesis. This ratio is indicative of the percentage of polymerizable structure, or ring content, in the whole composition without pointing out what kind of molecular structures these rings or bridges belong to. The \( CH_3 \) groups attached to the nitrogen atoms in the oxazine ring (b, chemical shift 2.33 ppm), or in the bridge structures (c, chemical shift 2.14 ppm) were also well resolved in the spectrum and could be used in the same way. Relatively pure difunctional bisphenol-A benzoxazine monomer was obtained by washing the composition with 3N NaOH solution. Components with free phenol groups in their molecular structures were either dissolved into aqueous solution or precipitated out of the ether phase during the washing operation. The composition and structure of the precursor after such treatment were confirmed by GPC and NMR spectrum (Figures 5,6).

Qualitative analysis of the structures of the dimers or higher oligomers can be obtained by a combined separation/spectroscopy methodology. This assessment is necessary to support the possible dimer structures outlined above and to further understand the reaction mechanism of the curing process. Three fractions were collected from the eluent during GPC analysis of the precursor, and highly sensitive UV and FTIR techniques were used to analyze the structures of the compounds in
each fraction of the eluent. The fractions were taken by considering the delay times for the eluent to transport along the line to the exit port after passing the detectors, and corresponded to retention times of 26-28.3, 28.3-29.7, and 29.7-32 minutes in the response of the UV detector. These collected fractions structurally corresponded to higher oligomers, dimers, and monomer respectively, and will be named bm1, bm2, and bm3 thereafter. UV spectra from 240 nm to 320 nm were obtained for them (in THF) along with the original solution (bm). The spectra are presented in Figure 3. While the monomer fraction bm3 shows predominantly one absorption at 282 nm, the original bm shows two maxima at 282 and 290 nm in its absorption. The 290 nm peak is found in fractions bm2 and bm1 together with absorptions at 282 nm. Thus, a rationale could be derived that bm1 and bm2 contain both benzoaxazine ring and free phenolic structures on the assumption that the maximum at 282 nm was due to the absorption by the benzoaxazine ring structures, whereas the maximum at 290 nm was due to the absorption of ortho-substituted phenolic structures.

For FTIR measurements, since the eluent solutions contain very low concentrations of the compounds, the solvent THF was allowed to evaporate first, and the nonvolatile residues were mixed with KBr powder. The mixtures were then ground to make KBr pellets for obtaining transmission spectra of the compounds. FTIR spectrum of the as synthesized B-m composition was collected from a thin film coated onto a KBr disc and is shown in Figure 4. Of interest here is the frequency region between 1550 cm\(^{-1}\) to 1400 cm\(^{-1}\) which contains the substituted benzene ring-modes which were different in the cyclic ring structure and polymeric linear bridge structures. The transmission spectra of bm, bm1, bm2, and bm3 in this frequency range are presented in Figure 5. The band at 1499 cm\(^{-1}\)
is attributable to the tri-substituted benzene ring-mode in the oxazine ring structure, while the band at 1481 cm\(^{-1}\) is assigned to the tetra-substituted benzene ring-mode in the ortho-substituted (methylene-amine-methylene bridge) phenolic structures formed by the reaction between the oxazine ring and the free ortho position of a phenol structure. The assignments were made with reference to the FTIR spectra of pure benzoazole compound and relatively pure aminomethylene bridged oligomers (its synthesis will be discussed in the next section) whose molecular structures were confirmed by their NMR spectra. It is also confirmed by FTIR band assignment on model compounds (13). The monomer component, bm3, shows essentially the benzoazole ring structure. The dimer and higher oligomer components, bm2 and bm1, show peaks due to both the oxazine ring and the free phenolic OH structures with an even higher number of free hydroxy groups in the bm1 component. Thus, while the majority of the composition after the synthesis is bisphenol-A benzoazole monomer, there are fractions of the composition with free phenolic hydroxy structures existing in dimers and higher oligomers which were formed by subsequent reactions between the rings and the ortho-position of bisphenol-A hydroxy groups. Furthermore, it also shows that these structures in the dimers and higher oligomers are capable of undergoing further reaction with formaldehyde and primary amine to reform the oxazine ring. The FTIR result is consistent with the structural feature of the precursor revealed by the NMR spectrum as shown in Figure 2, and mirrors the UV spectra of the three fractions of components shown in Figure 3.

This synthesis approach gives us complete conversion of the starting bisphenol-A into benzoazole and its higher oligomeric structures. The quantitative amount of monomer in the composition, assuming equal absorption coefficient for
the UV absorption groups in monomer, dimer, and higher oligomer structures, can be calculated by dividing the area under the monomer peak with the whole area of the chromatograph. This is understandably an estimation since the absorption coefficient is expected to change somewhat as the substitution structures on the bisphenol-A aromatic rings change. The response from the refractive index detector could be used in the same way under the assumption that the dn/dc of the solution kept constant for each of the components. The monomer content calculated by these methods was found to be 62% and 66%, respectively. It must be noted that the calculations yield weight percentage of the monomer in the composition instead of molar percentage. As pointed out before, another way to assess the composition is to obtain the ratio of the number of oxazine rings to those of the CH₂-N-CH₂ bridge structures which could exist in any of the dimer or oligomer structures by examining the corresponding CH₂ and CH₃ peaks in the proton NMR spectrum. The composition was found to contain 80% (84% from CH₃ groups) ring structures by this method. The existence of the dimers and higher oligomers with free phenolic OH structures is advantageous for initiating subsequent polymerization reactions. The composition will also determine the rheological properties of the precursor.

Effect of Solvent on the Precursor Composition

It was found that the composition of the synthesized benzoazine precursors depends, to a large extent, upon the nature of the solvent used for the synthesis. In dioxane, it has been illustrated in the last section that the majority of the composition is bifunctionally terminated bisphenol-A benzoazine monomer. The content of dimers and higher oligomers is at about 30-40% by weight of the composition. Different precursor compositions were obtained when the syntheses
were carried out in solvents with different polarity and solubility characteristics. In tetrahydrofuran (THF), the precursor was found to be predominantly dimers and higher oligomers. In methanol, the precursors precipitated out after half an hour at its reflux temperature. The precipitate filtered out at this time was found to be totally soluble in THF with essentially all higher oligomer compositions. The molecular structure of this oligomer was shown by NMR to be of almost all aminomethylene bridged structure whose FTIR spectrum was used as a reference for band assignment at 1481 cm\(^{-1}\) in the last section. If the reaction system was left uninterfered for a prolonged period of time (overnight), a mass precipitate was formed and found to be partially soluble with the majority being only swollen in THF. This indicated that a crosslinked network was achieved in the precipitate. With ethanol as the solvent, same result was observed. When 5 ml or 10 ml of acetic acid was added to the methanol solution at the beginning, a transparent, cross-linked gel was obtained which, after drying, was insoluble in all common organic solvents tested.

Figure 6 shows the GPC chromatographs of precursors obtained from THF and methanol solutions (the precipitated part of the precursor after half an hour of reaction in case of methanol) using the UV detector. Figure 7 shows the proton NMR spectra of these precursors. The increasingly lacking of benzoxazine ring structures in the precursor compositions is evident in the NMR spectra. Following the quantitative techniques illustrated in the last section, the amount of monomer in the precursor compositions were calculated. The results are tabulated in Table 1.

Table 1 suggests that as the solvent polarity increases, the reaction between the benzoxazine structures and the free phenol structures becomes easier. Thus, there are less benzoxazine rings present at the end of the reaction. This explanation
is based on the assumption that we always obtain the benzoxazine ring structures first before any of the substitution on the ortho positions of a free phenol can happen. This is supported by the fact that the bisphenol-A benzoxazine monomer always appears as the last component with the lowest molecular weight in the GPC chromatographs of the precursors. Dimerization of benzoxazines of the same reaction nature was documented in the literature (5).

The branching reactions are apparently part of the oligomerization process in the synthesis medium. This is quite natural and expected for the structure of the monomer which has four functionalities originating from the two benzoxazine rings at both ends of the bisphenol-A. The oligomeric components in the precursors synthesized in dioxane and THF would be consisted of both linear and branched structures. The formation of some kinds of macro-cyclic structures would also be possible. It seemed that solubility of the branched structures was maintained in the mixture of methanol and acetic acid solution so that a cross-linked network was eventually achieved, yielding a transparent gel structure in the solvent medium.

Materials from the Precursors

It has been shown in the past that phenols with free ortho position functioned as an initiator in the oligomerization of benzoxazine compounds. At elevated temperatures, the self-dissociation of the benzoxazine ring could also produce free phenol structures (10). A simplified scheme for the ring-opening reaction of a mono-functional benzoxazine initiated by a para-substituted phenol is shown below:

\[
\begin{align*}
\text{Ph} & \quad + \quad n \quad \text{Ph} & \quad \rightarrow \quad \text{Ph} \quad n
\end{align*}
\]
With difunctional or multifunctional benzoazine molecules, the resulting reaction products would be a cross-linked network.

The synthesis discussed in previous sections yields precursor with dimers and higher oligomers in the composition. These dimers and oligomers contain phenolic structures with free ortho positions as illustrated before, rendering the precursor to be self-initiating towards polymerization and crosslinking reactions. This is indeed advantageous for we can then cure the precursor into final part by simple thermal means. The rate of the curing reactions may also be controlled by controlling the composition of the precursor. Of course, addition of a certain catalyst would accelerate the reaction. Nevertheless, the precursor directly from the synthesis represents a good starting point for understanding the structure and properties of the materials.

The thermal characteristics of the curing process was studied by differential scanning calorimeter (DSC). An exotherm was observed which corresponded to the ring-opening reactions during the curing. In case of the precursor with 95% monomer content (as that obtained from dioxane synthesis and washed with NaOH solution) at a heating rate of 10°C/min, the exotherm starts at around 150°C. The peak exotherm occurs at 197°C and has an reaction enthalpy of -139 J/g. Since the molecular weight of B-m monomer is 340, this corresponds to a molar reaction enthalpy of -47.2 KJ/mole, or -23.6 KJ per molar benzoazine ring. The cooling cycle yielded no feature in the DSC curve, indicating that an amorphous, cross-linked structure was obtained in the heating cycle. The exotherm for precursor directly from dioxane synthesis has a maximum at 195°C. The reaction enthalpy is -104 J/g. The exotherm for precursor prepared in THF exhibited a feature of double exotherms with maxima at 185°C and 240°C, respectively. A
comprehensive DSC and TGA analysis of the curing processes of a series of difunctional benzoxazine compounds as well as the thermal stability of their resulting materials will be presented elsewhere (14).

Solid, rectangular samples of the cured materials were made from the precursors prepared in both dioxane and THF solvents by heating the precursors at 210°C for half an hour in a rectangular mold made of room temperature vulcanized (RTV) silicon rubber. Transparent, voidless, slightly brownish specimen were obtained. The specimens were then sanded down to desired dimensions with flat surfaces. A dynamic shear (torsion) mode was employed to study the viscoelastic response of the material. The strains applied were chosen to be within the linear viscoelasticity regime of the materials while providing reasonable torque responses. A heating rate of 3 °C/min was used in the temperature ramp from -140°C to 240°C. Figure 8 shows the dynamic mechanical spectrum of a cured phenolic sample made from the precursor synthesized in dioxane. The predominant loss peak at around 215°C corresponds to the glass transition temperature. Voidless sample from the precursor synthesized in THF solution was also prepared, with an extra effort to overcome the higher viscosity and faster reaction, by melting in the mold preheated at 140°C and apply vacuum to eliminate the trapped volatiles. The dynamic mechanical spectrum of this material is presented in Figure 9. Same features were obtained in the relaxation spectrum, indicating that similar cross-linked networks were obtained upon curing in spite of the differences in initial compositions. Since the precipitate from methanol consists of very little amount of benzoxazine ring structures in its composition, it was not attempted to process this composition.

CONCLUSION
By introducing bifunctionality in benzoxazine synthesis, using bisphenol-A in this study, useful benzoxazine compositions were obtained for the purpose of further curing into solid structures with the characteristics of phenolic materials. The components and their structures were analyzed by GPC, UV, and infrared spectroscopy. The composition of the precursor is consisted in majority of monomer with bifunctional benzoxazine ring structure at both end of the bisphenol-A. The rest of the composition consists of mixture of dimers and oligomers with both benzoxazine rings and free phenol structures present on a specific molecule. It is also shown that the composition of the precursors is, to a large extent, dependent on the polarity and solubility of the reaction medium or solvent. Furthermore, the compositions can be thermally initiated in curing into cross-linked structures characteristic of phenolic materials. The curing reaction is exothermic, the cured products exhibited good mechanical integrity and high glass transition temperatures.
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Table 2.1. Effect of solvent on the precursor compositions

<table>
<thead>
<tr>
<th>Solvent</th>
<th>monomer wt% (GPC)</th>
<th>ring content % (NMR)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UV</td>
<td>RI</td>
</tr>
<tr>
<td>Washed precursor</td>
<td>93</td>
<td>92</td>
</tr>
<tr>
<td>Dioxane</td>
<td>62</td>
<td>66</td>
</tr>
<tr>
<td>THF</td>
<td>35</td>
<td>38</td>
</tr>
<tr>
<td>Methanol</td>
<td>9</td>
<td>5</td>
</tr>
<tr>
<td>Methanol with acid</td>
<td>Crosslinked</td>
<td>Gel</td>
</tr>
</tbody>
</table>
Figure 2.1 GPC chromatograms of B-m and bisphenol-A
Figure 2.2  $^1$H-NMR spectrum of B-m
Figure 2.3  UV spectra of the original and collected fractions of B-m
FTIR spectra of original and collected fractions of B-m
Figure 2.6  GPC chromatographs of B-m precursors from dioxane and then washed (a), THF (b), methanol (c)
Figure 2.7  $^1$H-NMR spectra of B-m precursors from methanol(a), THF(b), dioxane and then washed(c)
Figure 2.8 Dynamic Mechanical Spectra of cured phenolic materials of B-m precursors from dioxane
Figure 2.9 Dynamic Mechanical Spectra of cured phenolic materials of B-m precursors from THF
Chapter III

EFFECT OF MOLECULAR STRUCTURES OF BENZOXAZINES
ON THE PROPERTIES OF THE PHENOLIC MATERIALS
INTRODUCTION

Conventional phenolic materials derived from condensation reactions in precursors of either novolac or resole type of resins exhibit the common shortcomings of brittleness and release of volatiles upon curing. The use of phenol also constitutes a threat to human health. Another disadvantage is the lack of molecular design flexibility imposed by the phenolic chemistry. This is apparent when one compares phenolic resins with epoxy, another category of thermoset materials with an extremely wide range of molecular design flexibility. It is not surprising, however, when there are only very few design molecules to build the structures, namely phenol, formaldehyde, and crosslinking agents like hexamethylene-tetraamine. The restriction on design further undermines the scope of the achievable material performances. These shortcomings are inherent to the phenolic chemistry. Therefore, complete solution to these problems cannot be achieved within the conventional phenolic chemistry.

In the previous chapter, it has been demonstrated that by introducing bifunctional or multifunctional benzoxazine precursors, crosslinked network structures with good mechanical integrity could be obtained. This approach eliminates the release of condensation byproduct upon curing and at the same time excludes the use of the toxic phenol. Equally or more importantly, it provides a chemical and structural framework with great molecular design flexibility and control of the curing reactions. Furthermore, because of the low molecular weight of the precursors, thus low viscosity, it offers a good opportunity for composite process design and manufacturing. The highly polar phenolic structures also make them ideal for composite binder applications. This chapter intends, as a first step in what is believed to be many aspects of molecular designs, to explore the effect of
chemical structures of the benzoazidine precursors on the mechanical and dynamic mechanical properties of the cured phenolic materials.

EXPERIMENTAL

The chemicals used in this work, namely biphenols, amines, formaldehyde, and dioxane were all purchased from either Aldrich or Fluka and used without further purification.

The syntheses were always carried out in dioxane with the reaction reagents of biphenols, formaldehyde, and primary amines in a molar ratio of 1 to 4 to 2. The detailed synthesis and molecular characterization processes have been described in Chapter II for bisphenol-A, methylamine (B-m) based precursor. The other six compounds described here followed the general synthesis procedure and their compositions and structures were analyzed in the same way by GPC, NMR and FTIR. The chemical structures of the difunctional benzoazine monomers and the abbreviations for their corresponding precursors that will be used throughout the text are illustrated in the following:

bisphenol-A based:
4,4'-dihydroxy biphenyl based:

4,4'-dihydroxybenzophenone based:

Tensile tests of the cured phenolic materials were carried out in an Instron-1123 instrument on dumbbell samples with specimen type M-III as specified in the standard for tension test of plastics (ASTM D638M). These sample specimens were prepared by curing at specified temperatures in an open mold made of room-temperature-vulcanization (RTV700) silicon rubber and were then sanded down to desired dimensions. The sanding process unavoidably produced surface flaws or
micro cracks in the material. The strength values thus obtained should be deemed as the lower limits of the material performances. The dynamic mechanical spectra of the cured phenolic materials were obtained on rectangular samples prepared in the same fashion as the tensile specimens. The experiments were carried out in a Rheometrics RMS-800 dynamic mechanical spectrometer from -140°C to above the glass transition temperatures, up to 280°C, at a heating rate of 3°C/min.

RESULTS AND DISCUSSIONS

Compositions of the Precursors

The as synthesized precursors include, in addition to the monomeric structures illustrated above, various amounts of dimers and higher oligomers in the compositions (1). These dimers and higher oligomers themselves consisted of a series of different isomeric structures that shared the structural characteristics of possessing both benzoazine rings and opened free phenolic groups. The molecular weight distribution of the precursors could be illustrated by their GPC chromatographs and the structural features identified by $^1$H-NMR and FTIR. Quantitative measurements of the composition of the precursors were obtained by GPC and NMR spectroscopy. The $^1$H-NMR spectra of these precursors are shown in the appendices to this chapter. Details of the composition analysis are referred to the previous chapter. The resulting compositions for the seven precursors are tabulated in Table 1.

It is evident from Table 1 that all the methylamine derivatives B-m, D-m, and O-m have higher percentage of dimer and higher oligomer structures than their aniline counterparts B-a, D-a, and O-a. This is because of the fact that the methylamine used in the synthesis was in the form of 30% methanol solution.
whereas aniline used was in an almost pure form. It has been shown in the bisphenol-A benzoxazine synthesis that the more polar methanol medium favors the formation of dimers and higher oligomers in the composition (1). Thus with the introduction of methanol to the syntheses of methylamine derivatives, a higher amount of dimers and higher oligomers were expected. By using aniline, however, the resulting precursors consisted of predominantly monomers as shown in Table 1. In addition to the effect of reaction medium, it is also probable that the basicity of the primary amines might play an important role in determining the composition of the precursors at the reaction conditions employed.

**Properties of the Cured Phenolic Materials**

The reactions between the heterocyclic benzoxazine ring and certain compounds HY, which have active hydrogens in their molecular structures, have been studied before (2,3). The ortho position in a free phenolic structure was shown to be active enough to initiate the ring-opening reaction of the benzoxazine ring. One additional free ortho position is generated once the ring is opened, thus carrying the reaction further in a chain-like fashion. A simplified reaction scheme for a mono-functional benzoxazine initiated by a para-substituted phenol is shown below:

\[
\begin{align*}
\text{Ph} & + n \text{Ph} \rightleftharpoons \text{Ph} \left\{ \text{Ph} \right\}_n \\
\text{(1)} & \text{(2)} \quad \text{(3)}
\end{align*}
\]

With difunctional or multifunctional benzoxazines, the resulting reaction products would be crosslinked networks. In systems under current investigation, the free
ortho positions of the phenolic structures were afforded by the dimer and higher oligomer structures in the composition, or alternatively, by self-dissociation of the benzoxazine rings at elevated temperatures (2,4). Through such reaction schemes, all the above listed precursors thermally cured into phenolic materials with good integrity and mechanical strength except the benzoxazine precursor based on bisphenol-A and cyclohexylamine (B-c).

In case of B-c, the material did not solidify after one hour at 190°C. When it was cooled down, a very fragile structure was obtained which easily broke into pieces. Melt viscosity measurements showed essentially no increase of melt viscosity (the viscosity stayed below the rheometer detection limit for reaction time up to one hour) for the isothermal reaction of the precursor B-c at 170°C although FTIR study did show reduction of the benzoxazine ring structures in the composition. The reactivity is, therefore, highly dependent on the molecular structure of the benzoxazine, and some side reactions might compete with the desired reaction path without leading to the formation of macroscopic structures during the curing. In this particular case, the substituent on the nitrogen atom of the benzoxazine ring seems to play a vital role in determining the reactivity of the precursors. The derivatives from methylamine and aniline, on the other hand, demonstrated ring-opening and crosslinking characteristics irrespective of the molecular structures of the biphlenol backbones.

FTIR spectra of the precursors and corresponding cured materials provided molecular information about the changes in chemical structures resulting from the curing reactions. Shown in Figure 1 are the FTIR spectra in the frequency region of 1600 cm\(^{-1}\) to 1200 cm\(^{-1}\) for the B-m precursor and its corresponding materials cured at 150°C and 200°C for 40 minutes. The absorption band at 1499 cm\(^{-1}\) and
1236 cm\(^{-1}\) are attributable to the benzoazole ring structure while the 1481 cm\(^{-1}\) band is related to the free phenolic structures resulting from the ring-opening reactions (1). The reduction of the 1499 cm\(^{-1}\) and 1236 cm\(^{-1}\) bands indicates the conversion of the benzoazole rings into phenolic structures. The reaction is, of course, dependent upon the curing conditions employed. For example, curing at 150\(^{\circ}\)C left a substantial amount of the 1499 cm\(^{-1}\) and 1236 cm\(^{-1}\) bands as shown in the same figure.

**Dynamic Mechanical Spectra of the Cured Materials**

The viscoelastic property of a polymeric material is a very useful link between its molecular structures and the macroscopic mechanical properties. One of the most often used techniques to obtain material viscoelastic properties is to subject a specimen to an oscillatory strain while detecting its stress responses, resulting in the so-called dynamic mechanical spectrum. For solid samples, it provides information about the movement and dynamics of molecules or molecular fragments. One of the most important parameters is the glass transition temperature of the material at a certain operating frequency. In addition, it provides the information about molecular relaxation processes below the glass transition and the rigidity of the material (modulus). With the possibility of systematically changing molecular structures of the materials, dynamic mechanical analysis would be a powerful tool in the study of structure-property relationships. The experiments under current investigation were carried out in a Rheometrics RMS-800 mechanical spectrometer with dynamic shear deformations being applied. The strains chosen were within the region of linear viscoelasticity of the materials while afforded reasonable torque responses throughout the temperature range. A typical strain value was 0.08\% for a sample dimension of 60x8x1.5mm.
1. Effect of Curing Temperature

Since each benzoxazine ring is bifunctional in terms of reactivity, the synthesized precursor molecules have at least tetrafunctionality which, upon ring-opening reaction with each other, form a highly crosslinked network. On the other hand, gelation and vitrification of the material depend on the temperatures at which the curing is carried out. Vitrification can occur during the reaction if the curing is carried out below the ultimate glass transition temperature of the material. Once it occurs, further reactions are controlled by diffusion processes where the network may grow through reactions with small molecular species diffused to the reacting localities. Under such conditions, complete conversion of the precursors to the network may be impossible. This is the reason why curing of B-m at 150°C left a substantial amount of unreacted benzoxazine rings as illustrated by FTIR spectrum shown in Figure 1. Thus, the curing temperature is very important in determining the final material structures formed. Figure 2 shows the spectra of dynamic shear modulus G* and loss factor tan δ of a phenolic material cured from B-m precursor at 200°C for 40 minutes. The transition at the highest temperature is the glass transition. Below that there are some relaxation activities from room temperature up to about 100°C (the broad shoulder) which we may tentatively call β transition and, around -90°C, the γ transition.

Loss tan δ spectra of several B-m based phenolic materials cured at various temperatures (150, 180, 200, 236 °C) are shown in Figure 3. It is evident that the glass transition temperatures greatly depend upon the curing temperature, a result expected from the above discussion. It is also noted that the absolute values of the tan δ in the β region were higher for material cured at lower temperature than that cured at higher temperatures, indicating that the material cured incompletely has a
greater amount of viscous components in its structure. The glass transition
temperatures for the B-m series materials are plotted in Figure 4 as a function of
curing temperature. The ultimate Tg achievable was found to be 215°C. This
represents complete conversion of the precursors into the network structure, and
thus, the Tg is determined only by the chemical structures of the network. Curing
at 200°C for 40 minutes resulted in a Tg value higher than the curing temperatures
employed. One possible reason for this is that the reaction exotherm might have
caus[ed the actual temperature in the mold to be higher than that indicated. It is also
possible that further crosslinking reactions after its vitrification point might occur to
drive the Tg of the material above the curing temperature. This would not be
surprising when considering the molecular size of the B-m monomer and the
addition mechanism of the curing reaction. The vitrified state at the curing
temperature probably still possessed enough free volume for the diffusion of the
small B-m monomer to reach the reaction sites, driving the curing reaction to
completion. The γ process at low temperature, on the other hand, did not seem to
be influenced by the difference in curing temperatures and stayed reasonably
constant around -90°C. This will be understandable when we assess its mechanism
of the local molecular motions in the following section.

2. Effect of Molecular Structures of the Precursors

The effect of the substituent attached to the nitrogen atom on the reactivity of
benzoxazine precursors based on bisphenol-A was briefly discussed in previous
section. With cyclohexyl group (B-c), the reactivity towards formation of
macroscopic structures was hindered, and no hard material was obtained. With the
methyl substituent on the amine (B-m), the resulting network showed an ultimate
glass transition temperature of 215°C. Figure 5 illustrates a dynamic spectrum of a
material cured from precursor B-a at 220°C for one hour. The ultimate Tg was found to be 190°C with the γ process occurring at around -70°C. The dynamic relaxation spectra for materials from the other two linear biphenols, 4,4'-dihydroxy biphenyl and 4,4'-dihydroxybenzophenone, are presented in Figure 6 and Figure 7. The materials were obtained at a curing temperature of 220°C for one hour. It is noticeable that the general feature of the spectra of the phenolic materials remains the same in spite of the differences in backbone chemical structures. One still observes three transitions in the temperature range probed. The positions of the Tg seem to be the most sensitive to chemical structural changes. In D-m, D-a series, again the methyl substituent provided material with a higher Tg than its counterpart from the phenyl substituted D-a. The highest Tg, however, was obtained in materials from the benzoxazine of 4,4'-dihydroxybenzophenone and aniline (O-a) which showed a respectable Tg of 266°C, while its methyl counterpart showed a Tg of 237°C. It is also quite noticeable that the Tg of the materials exceeded drastically the curing temperature employed (220°C). This is believed to be due to the same reasons outlined in the previous section. Similar phenomena were reported in the literature before for thermosetting materials such as epoxies.

It was also noted that the materials from methylamine (B-m, O-m, D-m) degrade at around 280°C. TGA studies showed that it is probably related to the cleavage of the methyl groups on the tertiary amine structures. With aniline derivatives (B-a, O-a, D-a), the degradation temperatures could be up to 350°C. Detailed degradation behaviors are discussed elsewhere (5). The α and γ transition temperatures at 1 Hz for the phenolic materials cured from the six different precursors are listed in Table 2.
Dynamic mechanical behaviors of conventional phenolic materials have rarely been reported so far in the literature. This is probably due to the fragile nature of the conventional material and the fact that most commonly supplied phenolics are highly filled systems. The current benzoxazine system not only offers good mechanical integrity for dynamic mechanical analysis, but also provides the flexibility of molecular design to systematically change the structural variables. The $\gamma$ relaxations at low temperatures showed good correspondence for some structural characteristics in materials cured from different precursors. It seems that there is a coincidence of the $\gamma$ peak positions for a certain structural feature. For materials with methyl substituent on the nitrogen atoms, the $\gamma$ peak position occurred at lower temperatures (B-m, -90°C, D-m, -81°C, O-m, -94°C). Materials with phenyl substituent on the nitrogen atoms, on the other hand, exhibited $\gamma$ peak positions at almost the same, but higher than that of their methyl substituted counterparts, temperatures (B-a, -70°C, D-a, -75°C, O-a, -76°C). It is thus reasonable to believe that there is a correlation between the $\gamma$ processes of the crosslinked network and the thermal motions of the pendant groups attached to the nitrogen atoms. These results also show that the motions of the pendant groups, irrespective of the backbone structures, are activated at lower temperature for the smaller sized groups (like methyl) than for the more bulky groups (like phenyl) as reflected in the peak maxima of the $\gamma$ relaxations.

As for the nature of the $\beta$ process, it was noted that the amplitude of the $\tan\delta$ of the $\beta$ relaxation consistently decreased with improved curing conditions. However, there was still a quite noticeable shoulder even after the material has reached the ultimate $T_g$ of the system. For all the materials from the six different precursors, the shoulder feature of the $\beta$ relaxation always remained and actually
occurred in approximately the same temperature range. If they were due to the unreacted precursors, we would expect that they occur at different temperatures since the physical properties of the precursors are very different. The notion of an incomplete network structure seems more acceptable. The great variety of the intermediate structures that are not completely incorporated into the network could be responsible for the broad nature of the β relaxation.

**Mechanical Properties**

The stress-strain behavior is one of the most useful source of information for material application purposes. It provides the information about material stiffness (Young’s modulus), strength, and some indication of the toughness (the energy to fail the material) under the loading conditions. Traditionally, the mechanical properties of pure phenolic materials have been lacking, due to the fragile nature of the conventional phenolic materials. The formation of microvoids in the product due to the generation of condensation byproducts (water, ammonia, etc.) upon curing further deteriorates the material integrity. As a matter of fact, unfilled system was deemed to be of little engineering significance. (6) Tensile strength values for various filled, or reinforced phenolic materials ranging from 48 to 148 MPa were reported. (7) Some of the commercially available filled phenolic materials showed tensile strengths at 30-50 MPa. (8)

Transparent, voidless tensile specimens with good mechanical integrity were prepared by curing the precursors in an open mold. In ASTM D638M tensile test, five or more specimens should be tested in order to give a statistically reliable result. In the current practice, however, only one or two specimens were tested due to limitation imposed by available quantity of the precursors. Otherwise, the test procedures of D638M including sample conditioning were followed. The test
speed was set at 0.5 mm/min for the M-III type specimen. Figure 8 shows the stress-strain curves of materials cured from B-m, B-a, D-a, and O-a, respectively. Samples from D-m and O-m failed in the grips. The numerical values generated from these curves are presented in Table 3.

The typical strength values of these materials were apparently superior to conventional phenolic materials. The combination of strength and heat-resistance (Tg) demonstrated that they could also be compared quite favorably with some of the widely used high performance epoxy materials. At the testing strain rate, the stress-strain curves are essentially linear with elongation at break at around 2%. Among those new structures, the material from O-a again championed the performance with the highest strength value and elongation at break, though the highest modulus was obtained for material from D-a.

CONCLUSIONS

The reactivity of the benzoxazine precursors to form crosslinked structures seems to be determined by the substituent group on the nitrogen atom in the benzoxazine ring. Precursors from methylamine and aniline exhibited good reactivity towards ring-opening reactions to form crosslinked phenolic structures.

The effect of molecular structure on the glass transition temperatures was illustrated. By designing the molecular structure of the precursors, and therefore the structure of the crosslinked network, different performance on heat-resistance can be accomplished. The molecular origin of the γ relaxations in the new phenolic material systems was related to motions of the pendant groups attached to the nitrogen atoms in the crosslinked structures.
Finally, the preliminary results on the mechanical properties of the phenolic materials based on the current synthetic approach have shown that there is a great potential of developing this category of materials into low cost, high performance thermoset materials with good handling capability for material processing and composite manufacturing.
REFERENCES

1. chapter II of this thesis.


4. chapter IV of this thesis.

5. H. Ishida, and X. Ning, to be published.


Table 3.1. Compositions of the synthesized precursors

<table>
<thead>
<tr>
<th>Precursors</th>
<th>monomer wt% (GPC)</th>
<th>ring content% (NMR) *</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UV</td>
<td>RI</td>
</tr>
<tr>
<td>B-m</td>
<td>62</td>
<td>66</td>
</tr>
<tr>
<td>B-a</td>
<td>79</td>
<td>77</td>
</tr>
<tr>
<td>B-c</td>
<td>75</td>
<td>77</td>
</tr>
<tr>
<td>D-m</td>
<td>80</td>
<td>78</td>
</tr>
<tr>
<td>D-a</td>
<td>96</td>
<td>95</td>
</tr>
<tr>
<td>O-m</td>
<td>85</td>
<td>/</td>
</tr>
<tr>
<td>O-a</td>
<td>97</td>
<td>96</td>
</tr>
</tbody>
</table>

* calculated by the resonance area of CH₂ and CH₃ peaks corresponding to benzoxazine rings and bridge structures (1)
Table 3.2. Transition temperatures (°C) of the phenolic materials from different precursors at 1 Hz

<table>
<thead>
<tr>
<th>Precursors</th>
<th>$\alpha$ (°C)</th>
<th>$\gamma$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-m</td>
<td>215</td>
<td>-90</td>
</tr>
<tr>
<td>B-a</td>
<td>190</td>
<td>-70</td>
</tr>
<tr>
<td>D-m</td>
<td>243</td>
<td>-81</td>
</tr>
<tr>
<td>D-a</td>
<td>228</td>
<td>-75</td>
</tr>
<tr>
<td>O-m</td>
<td>237</td>
<td>-94</td>
</tr>
<tr>
<td>O-a</td>
<td>266</td>
<td>-76</td>
</tr>
</tbody>
</table>
Table 3.3. Tensile properties of the phenolic materials from different precursors (test rate 0.5mm/min)

<table>
<thead>
<tr>
<th>Precursors</th>
<th>E (GPa)</th>
<th>$\sigma_b$ (MPa)</th>
<th>$\varepsilon_b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-m</td>
<td>3.1</td>
<td>59.8</td>
<td>2.1</td>
</tr>
<tr>
<td>B-a</td>
<td>3.2</td>
<td>58.2</td>
<td>1.9</td>
</tr>
<tr>
<td>D-m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D-a</td>
<td>4.2</td>
<td>67.7</td>
<td>1.7</td>
</tr>
<tr>
<td>O-m</td>
<td>3.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O-a</td>
<td>3.6</td>
<td>78.2</td>
<td>2.3</td>
</tr>
</tbody>
</table>

$\sigma_b$: strength  
$\varepsilon_b$: strain at break
Figure 3.1 FTIR spectra of the B-m precursor and cured materials
Figure 3.2 Dynamic mechanical spectrum of cured B-m
Figure 3.3 Dynamic loss spectra of materials cured at different temperatures from B-m
Figure 3.4  Tg dependence on curing temperature
Figure 3.5
Dynamic mechanical spectrum of cured B-a
Figure 3.6  Dynamic mechanical spectra of cured D-m and D-a
Figure 3.7 Dynamic mechanical spectra of cured O-m and O-a
Figure 3.8  Stress-strain curves of phenolic materials
3. A3  $^1$H-NMR spectrum of D-m
Chapter IV

RHEOLOGICAL ANALYSIS
ON THE CURING KINETICS AND STRUCTURES
INTRODUCTION

The study of the changes in rheological properties resulting from chemical reactions has been collectively called chemorheology. It was originated by Tobolsky in the analysis of chain scission and degradation of rubber materials by stress relaxation behaviors (1). The rheological characteristics of thermosetting resins during the curing process is of great importance in both scientific understanding of the reactions and engineering application for the materials (2,3). In addition to the kinetics of the structural buildup, detailed analysis can provide information concerning the structures of cured materials by examining their relaxation and/or equilibrium properties.

In the processing of thermosetting resins, the change of the structures during curing is manifested by an increase in viscosity. Such structural buildup is the result of chemical reactions which lead to increased molecular weight, branching, and crosslinking. However, the kinetics of viscosity increase does not directly correspond to the kinetics of the chemical reactions. It is important to investigate the structural and rheological changes since the material flow and shaping capabilities are determined by such changes. The study of macroscopic changes can also contribute to the understanding of the chemistry and kinetics of the reactions.

During the structural evolution of the material, the determination of the gel point at a certain reaction temperature has the single most important significance in the processing of thermosetting materials. The definition of the gel point is relatively straightforward. It may be stated accurately as the point where the steady shear viscosity of the material becomes infinite while the long term equilibrium modulus is zero. However, the practice of identifying the gel point has been
experimentally difficult and the techniques far from universal. Traditional industrial practices of observing the flow or bubbling do not lead to much scientific understanding or even resolve the ambiguity associated with gelation (4). During the past several years, more objective techniques have been advanced. Gillham pioneered the Torsional Braid Analysis (TBA) and used it to study the curing of thermosetting resins. He and co-workers identified the gel and vitrification points and further established a general protocol called Time-Temperature-Transformation (TTT) diagram for crosslinking systems (5-7). In this technique, a damping maximum in the TBA spectrum was identified as the gel point and a later damping maximum as the vitrification point. However, it is realized that the first damping maximum might be a composite effect instead of a property of the curing material itself due to the existence of fiber filaments in TBA experiments (8). Dielectric damping response of a curing system have also been used in a similar fashion (2). These techniques, though convenient and visually easy to accept, lack solid theoretical interpretation of the phenomena.

The dynamic measurement of the evolution of the storage modulus $G'$ and loss modulus $G''$ with a rheometer was first found to be a convenient way to monitor continuously the entire curing process and their crossing point was found to be closely associated with the gel point of the system (9,10). A simple constitutive gel equation was proposed to describe the dynamic and relaxation behavior of cross-linking systems with an end-linking mechanism (11) in which it was found that for polydimethylsiloxane (PDMS) system with exact crosslinking stoichiometry, the condition of congruency $G'(\omega) = G''(\omega) (0 < \omega < \infty)$ fulfils all the criteria set forth for a gel transition. The constitutive equation contains only one material parameter (gel strength $S$) and the corresponding stress relaxation modulus
follows simple power law equation \( G(t) = St^n \) where \( t \) is relaxation time and \( n \) equals \( 1/2 \) for stoichiometric end-linking. For systems with non-stoichiometry, the congruency condition could not be fulfilled. Consequently, the power law relaxation modulus relation had \( n \) values greater than \( 1/2 \), and the gel formation occurred prior to the \( G',G'' \) crossing point at the operating frequency described in that case (12).

In previous chapters, the chemistry and material characteristics of phenolic materials cured from difunctional benzoxazines via a ring-opening polymerization process have been explored (13,14). Benzoxazine-based phenolic resins have demonstrated many advantages over conventional phenolic resins which utilize precursors of either novolac or resole type. This study intends to examine the rheological properties of these systems during cure in light of the aforementioned principles, supplemented by experiments to probe the structures of the cured materials.

The systems in the current investigation differ from the systems studied before in at least two aspects. First, the reaction temperatures were below ultimate \( T_g \) of the materials, thus vitrification would play an important role of determining the time during which experiment could be carried out and its effect may be realized in the rheological behavior of the systems. Second, the crosslinking mechanism is more addition type reactions than the conventional condensation reactions encountered in epoxy or PDMS systems. However, It is necessary that the experiments be carried out at temperatures below the ultimate \( T_g \) of the material since the reaction would simply be too fast to follow experimentally at higher temperatures, as is the case encountered for most of the high performance, heat-resistant thermoset materials. It is also rational to do so as long as the influences
imposed by vitrification and other factors are either excluded or taken into consideration. Thus, the first objective in this study is to observe the dynamic viscosity evolution of two systems at different temperatures before reaching the vitrification point. Secondly, an examination of the applicability of the dynamic $G'$, $G''$ evolution approach for the determination of gel point in this phenolic system below the ultimate $T_g$ of the material will be discussed. Finally, the structures of the curing materials will be probed with stress relaxation and solubility experiments.

EXPERIMENTAL

The synthesis and composition of the phenolic precursors studied here were discussed in previous chapters (13, 14). The two precursors were all based on bisphenol-A and have difunctional benzoxazine monomeric structures shown below:

![B-m monomer](image)

(B-m monomer)  

![B-a monomer](image)

(B-a monomer)

Their corresponding precursors are abbreviated as B-m (from bisphenol-A and methylamine) and B-a (from bisphenol-A and aniline) respectively throughout the text. The precursors were shown to consist mainly of monomers with dimers and higher oligomers accounting for 36% by weight for B-m and 22% by weight for B-a(14). The difference in composition was due to differences in synthetic
conditions. The structures and functions of the dimers and higher oligomers are discussed in the previous chapters (13.14).

The rheometer used was a Rheometrics RMS-800 mechanical spectrometer in parallel plate geometry with 25 mm-diameter aluminum plates and 0.5 mm gap. The instrument is equipped with a force-rebalance transducer with an operating torque range of 0.5-1600 gram-cm. A forced air convection oven with independent thermocouples for control and readout was used for optimum temperature stability. The temperature fluctuation during the experiment was approximately ±0.5°C. The experiments employed included isothermal cure experiments and stress relaxation experiments. In the isothermal cure mode, the storage modulus $G'$, loss modulus $G''$ and the loss factor $\tan \delta$ were monitored as a function of curing time at different temperatures with oscillation frequency of 10 Hz and 5% strain. The frequency was chosen to enable the relatively fast data acquisition necessary at higher temperatures. In the stress relaxation mode, a step strain of 2% was applied and the stress relaxation of the material recorded in three time zones of durations 1, 10, 110 seconds with 512 data points collected in each zone. At the sample geometry, the 2% strain corresponded to a radial displacement of 0.8 milli-radian which the rheometer motor is capable of performing in far less than 10 milli-seconds. Thus, the relaxation spectra in the time domain after 10 milli-seconds are reliable experimental data. The oven was preheated at each temperature to set the zero gap. After loading the sample, the oven was closed and the temperature was preset at 30°C below the desired temperature to reduce the temperature overshoot. The temperature was then raised and the experiment started one minute after reaching the desired temperature. It was understood that such handling could introduce temperature inhomogeneity at the initial stage of the reactions.
RESULTS AND DISCUSSIONS

Isothermal Curing Process

Curing of the precursors B-m, B-a into phenolic structures involves the ring-opening reaction of the benzoxazine rings. This ring-opening reaction is initiated by the ortho positions of free phenolic structures as schematically shown below for a mono-functional benzoxazine compound:

For difunctional benzoxazines as B-m and B-a, the resulting structure would be a cross-linked network.

In current precursor compositions, the free phenolic initiating species were offered by the dimers and higher oligomers. It was reported previously that the self-dissociation of the benzoxazine ring at elevated temperatures could also offer such initiating species(16). To maintain predominantly a single reaction mechanism in the experiments, the contribution from self-dissociation was assessed by isothermal curing experiments of pure B-m and B-a monomers. The purification was done by washing the ethyl ether solutions of the precursors with 3N NaOH aqueous solution. Any of the molecules in the composition with free OH groups in the structures were converted to sodium salt form which was either soluble in water or precipitated out of the organic ether phase. It was found that the viscosity of the pure monomer curing systems, at temperature up to 170°C for B-m and 180°C for B-a systems, were still below the transducer sensitivity level after equivalent reaction times in the precursor experiments (torque value below 0.5 gram-cm in
comparison with around 300 gram-cm at the end of the precursor curing experiments). Thus, even if there was self-dissociation at the reaction temperatures, the contribution from such initiated curing was negligible during the time span in the experiments at temperatures lower than those indicated above.

As was stated in the last section, vitrification plays an important role in curing at temperatures lower than the ultimate Tg of the material (Tg*). The Tg* is determined only by the network chemical structures and represents complete conversion of the precursors. If the curing reaction is carried out at temperatures Tcure higher than Tg*, the reaction will continue to completion without any physical interference. However, at temperatures lower than Tg*, the network vitrifies when its Tg becomes equal to the curing temperature Tcure. After vitrification further reactions are still possible but are hindered dramatically by diffusion process. Since the material becomes very rigid and contracts upon vitrification, the rheometer transducer is no longer capable of response in the parallel plate geometry. Thus the experiments were stopped when the tan δ started to increase to protect the transducer, and also to discard the faulty data. By doing so only the process before vitrification are observed. This time period may or may not include the chemical gelation point of the curing system depending on the gelTg (Tg of the network at gelation point) of the material. If gelTg = Tcure, gelation and vitrification occur simultaneously. Thus curing under Tg* involves the understanding of the relationships among network instant Tg, Tg*, gelTg, and Tcure. It was shown in chapter III that curing of B-m at 150°C left substantial amount of unreacted benzoazines in the cured resin. These characteristics and their influence on rheological measurement are the subject to be explored further in
this chapter. From previous work, the Tg* of B-m and B-a systems have been identified as 215°C and 190°C respectively.

Figure 1 shows the evolution profiles of the dynamic viscosity in the B-m isothermal curing experiments before reaching the vitrification point at each temperature. For temperatures at or lower than 120°C, the G' and G" did not cross over each other before vitrification. For temperatures higher than 170°C, the reaction was too fast to obtain a reasonable amount of data, and the contribution from the self-initiation becomes substantial. It is apparent from this figure that the viscosity increase is a continuous function with no indication of whether there has been a gel point during its evolution. This is consistent with previous suggestions that chemical gelation corresponds to a gradual physical transition, it does not cause an abrupt macroscopic change, nor alter the speed of the curing reaction (5,11).

Figure 2 is a curing profile of B-m at 140°C. It is typical of the curing evolution curves where storage modulus G', loss modulus G", and loss tanδ are plotted against time. At the beginning, the precursor had very low viscosity so that the torque response for 5% strain was below the transducer sensitivity range and the G' and tanδ data points were not reliable. As the curing reaction proceeded and viscosity increased, the data began to fall within the transducer sensitivity range and the G" was shown to be much higher than the G', indicating the fluid nature of the system. As the internal molecular structures built, the elastic component G' started to increase more rapidly than the G" and eventually surpassed the G" curve. At the same time the tan δ values of the curing system monotonically decreased.

Figure 3 shows the curing profile at 150°C. Due to a faster reaction rate, the slopes of G', G" curves are steeper and the time it takes to reach the G', G" crossing point is reduced. Gelation theory dictates that, at the gel point, the material
has the same conversion (and thus iso-structure if the reaction path or mechanism is the same) for a specific crosslinking system regardless of the temperature of the curing reaction (15). Thus it is an iso-conversion property of the system itself. Mathematically, one may write for any reaction order:

\[- \frac{dX}{dt} = kX^n\]

the chemical conversion at the gel point \((X_0 - X_g)\) is a constant for a given system:

\[- \int_{X_0}^{X_g} \frac{dX}{X^n} = kt_{gel} = \text{constant}\]

\[k = \text{constant} / t_{gel} = A e^{-\frac{E_a}{RT}}, \quad \ln t_{gel} = C + \frac{E_a}{RT}\]

The kinetic constant of the reaction, \(k\), should follow an Arrhenius relationship with reaction temperature if there was only one reaction path. If one takes the \(G', G''\) crossing point as the gel point, the activation energy of the overall chemical reaction can be calculated by plotting log time to gelation, \(\log t_{gel}\), against the reciprocal curing temperatures. Gelation times determined by dynamic experiments at different temperatures are presented in Table 1. The Arrhenius plot is shown in Figure 4 and the activation energy is found to be 25 kcal/mole. This value was higher than a previously suggested value of 16 kcal/mole obtained by NMR analysis on a model mono-functional benzoxazine reaction initiated by a 2,4-tertiary butyl substituted phenol (16). In addition to the different molecular structures of benzoxazines (the reactivity of the two rings in B-m might also be different) and initiating species used, the difference in experimental techniques (one macroscopic
while another molecular) was thought to be responsible for the disagreement in the values. The good linearity in Figure 4 indicated that there was indeed only one predominant reaction mechanism involved in the temperature window, namely the initiation by the dimer or higher oligomers followed by propagation, branching and crosslinking.

To ascertain if the $G'$, $G''$ cross-point did indeed correspond to the true chemical gel point, stress-relaxation and solubility experiments were performed. Both confirmed that true continuous gel structures were formed after the $G'$ and $G''$ cross point (details in the following section). From these experiments, it is apparent that the $gel_Tg$ of the B-m system is lower than the curing temperatures $T_{cure}$ used so that the gelation could occur during the dynamic experiments before vitrification occurred. It is understandable that the dynamic assessment could be used under such a situation since the gelation occurred reasonably away from the onset of vitrification and there were no other physical forces such as phase separation or physical entanglement in the sample. Although the curing system in the current investigation (B-m) did not meet the requirements set forth in earlier work for the gel point to be exactly equal to the $G'$, $G''$ crossing point (11), it seemed that it behaved reasonably well to occur in the vicinity of the crossing point at the operating frequency.

One also notices that by the end of the experiments, the tan $\delta$ values did not change very much and their magnitudes were lower at higher reaction temperatures than at lower temperatures as shown in Table 1. This trend is illustrated in Figure 5. This phenomenon is due to the fact that at higher reaction temperature, the curing system had higher chance to further react in the gelled state before the system reaches vitrification and thus the resulting system would have higher conversion.
Consequently, they would contain higher amount of elastic structures and lower amount of viscous reaction intermediates at the onset of vitrification. In other words, it would better approach the structure defined by the material T_{g^*} at higher T_{cure}.

The same methodology could be applied to the isothermal curing reactions of the B-a precursor as presented in Figure 6 through 8. Figure 6 is the viscosity evolution curves at different curing temperatures. Figure 7 is the isothermal curing profile at 160\(^\circ\)C showing the structural evolution of G', G'' and tan\(\delta\). The times at which G', G'' crossover occurs are also tabulated in Table 1. Figure 8 is the Arrhenius plot of the log time to G',G'' crossing versus reciprocal temperature. The data points, however, deviated from an ideal linear line and were somewhat curved. In the following section, it will be shown that the G',G'' crossing point in B-a isothermal curing experiments did not correspond to the true chemical gel point. Therefore, the data manipulation for activation energy used in B-m system would not be applicable in the B-a system.

The Stress Relaxation and Solubility Experiments

Stress relaxation experiments were carried out in order to probe the structural build-up in the melt during the isothermal curing process before the vitrification point. They were also designed to assess the assignment of gel formation at the crossing point of the G' and G'' curves in the dynamic experiments. Since each experiment lasted for two minutes, successive experiments were carried out in three-minute intervals, leaving a one-minute delay time before starting the next step strain. Experiments were also carried out for B-a material above its ultimate T_{g^*} to bypass the vitrification effect.
The 2% strain was found to be within the linear viscoelastic region up to the onset of vitrification. It was also believed to be small enough to have no damage effect on the gel structures in the curing system. This was supported by the fact that the initial value of the relaxation modulus G(t) kept increasing as the curing continued. In Figure 9 the relaxation moduli G(t) across the time span for B-m curing at 150°C are presented at the time interval of every three minutes. At the beginning of the cure(Curve 1,2 at 6 and 9 minutes), the G(t) rapidly decayed to below the transducer sensitivity level, indicating that there was no permanent structure in the system. As the isothermal cure continued, the average molecular weight increased so that the slope of the G(t) curve became flatter (correspondingly, the average relaxation time \( \tau \) became larger) from curve 1 to curve 2. At time 12 minutes, an equilibrium modulus appeared, suggesting the emergence of a permanent structure, namely the gel structure in the fluid. Thus the gel point must have been reached between the relaxation experiments 2 and 3 or between time 9 and 12 minutes. This agreed well with the time of \( G' \), \( G'' \) crossing point at 10.0 minutes in dynamic measurement. As the chemical reaction continued to form more cross-links in the gel, the structure became more rigid with the equilibrium modulus \( G_\infty \) values increasing correspondingly. No apparent relaxation was observed in the two-minute time span when the system started vitrifying by the end of the experiment. The exact moment when there was a permanent structure formed in the fluid was difficult to determine by the stress relaxation experiments since each individual experiment took two minutes to finish and then there was a one minute delay time. The gelation point could be reached at any moment during this time period. Thus the stress relaxation experiments could only provide a rough estimate of the time for gel formation which in this case included the \( G' \), \( G'' \) crossing point.
Even so, it was still comforting and gave credence to the use of the $G'$, $G''$ crossing points as gel points to draw activation energy of the curing reactions in the previous section. The evolution of the equilibrium modulus $G_{\infty}$ in the gel state indicated that the stress relaxation experiment is an ideal tool for probing the build-up of the gel structures during the curing reaction.

Qualitative solubility experiments also confirmed the gel formation. The solvent dimethylsulfoxide (DMSO) was found to have the best dissolving capability among strong organic solvents tested. At 120°C there was no $G'$, $G''$ crossover before the material started to vitrify. Consistently, the solidified material was found to be completely soluble in DMSO at 100°C. Other solvents could not dissolve it at similar conditions. Thus DMSO was chosen as the probe for gel structures. For isothermal experiments at 131°C and higher, $G'$, $G''$ crossover were always observed before material vitrification. Consequently the solidified materials could not be dissolved completely in DMSO at 100°C for 10 hours, indicating that continuous network structures had been formed in the materials cured at these temperatures.

Figure 10 illustrates the stress relaxation moduli of B-a system for different reaction times at a curing temperature of 160°C. The evolution of the $G(t)$ curves exhibited a very different behavior than that of the B-m system. The relaxation moduli at the beginning of the reaction(curves 1, 2 at times 15, 18 minutes) were the same as in the case of B-m with rapid decaying of stress. Then a plateau in the $G(t)$ curve emerged which, however, was further relaxed by a secondary relaxation process. The transformation from straight stress decay to the emergence of a plateau occurred between the time 18-21 minutes which happened to include the $G'$, $G''$ crossing point at 19.8 minutes. As the reaction continued, the modulus values
at the plateau increased and the plateau region widened. However, the secondary relaxation still occurred within the two-minute time span to make the sample fully comply with the imposed strain. In the relaxation time domain, the first relaxation happened within 100 milli-seconds after the step strain, while the secondary relaxation happened in the time domain of one second to tens of seconds. Similar relaxation spectra were also encountered at a curing temperature of 170°C as illustrated in Figure 11. The complete decay in the secondary relaxation indicated that there were no infinite, macroscopic structures in the material cured at 160°C and 170°C even though the material's elastic component dominated the dynamic response after the $G'$, $G''$ crossing point in the dynamic experiments.

In order to exclude the effect induced by material vitrification, stress relaxation experiments were carried out at temperatures of 220°C and 240°C, which are 30 and 50°C higher than the $T_g^*$ of the B-a system (14). In consideration of the fast reaction rate at these high temperatures, the sample and fixtures were actually loaded at 160°C, then the temperature was raised to 220°C or 240°C respectively. The experiments started five minutes after the oven reached the desired temperatures, thus the first experiment started at an arbitrary reaction time when the plateau in the relaxation moduli had already appeared. The relaxation spectra at 220°C and 240°C are presented in Figures 12 and 13. They are consistent with previous experiments at 160 and 170°C in that there still were secondary stress relaxations at the beginnings of the curing processes even though the temperatures were considerably higher than $T_g^*$. Thus, the feature of dual-step stress relaxations at lower temperatures could not be an effect induced by potential vitrification. As the reaction time progressed, however, the relaxation plateaus at
220 and 240°C were extended to longer time domains and equilibrium moduli were eventually developed, indicating the formation of chemically crosslinked network.

The solubility test was again used to examine the structures of the cured materials which showed the $G'$, $G''$ cross over in the dynamic experiments while exhibiting dual relaxation behavior in the stress relaxation experiments. The materials from B-a after the 160°C and 170°C isothermal curing experiments were found to be completely soluble in DMSO at 100°C and they remained clear solution after being cooled down to room temperature, suggesting that only finite structures were present in the cured resins. As mentioned previously, materials cured from B-m at 131°C or above did not dissolve under the same solvent condition and corresponded to continuous macro-gel state as illustrated by the stress relaxation experiments. It is apparent that the B-a materials cured at 160°C and 170°C were not in such state. The eventual decay to zero modulus in stress relaxation experiments is thus apprehensible since there was no infinite network formed under such conditions. Therefore, the behavior of dual relaxations and $G'$ dominance in dynamic experiments had to be explained in terms of finite structures.

The structure of the B-a materials cured at 160 and 170°C, judging by evidences presented so far, could be either a microgel or a physical gel. The concept of micro-gel had been proposed for certain epoxy curing systems (17). It might be responsible for the results of both the solubility and stress relaxation experiments while maintaining the chemical gelation nature within each microgel domain. Thus, it is possible that the microgel assembly could be broken up in certain solvent to form a transparent colloidal solution, indistinguishable from a true solution if the particle sizes were smaller than the wavelengths of visible light. In the dynamic experiment at the oscillation frequency of 10 Hz, the microgel
structures could exhibit higher elastic than viscous characteristics or behave like a gel. But in longer time domain at the stress-relaxation experiments, the assembly of these microgels could be deformed under stress due to limited inter-particle forces, thus generating the secondary stress relaxations. Even the phenomenon of the eventual appearance of equilibrium modulus at higher temperatures could be explained as the result of subsequent chemical reactions between the micro-gel particles as the reaction continued. The only way to differentiate a micro-gel from a physical gel was to determine if the DMSO solution was a colloidal solution or true solution.

The DMSO solutions of the B-a material cured at 160°C and 170°C were filtered through Teflon membranes with 0.45 μm pore size. The dried membranes were weighed to determine if there were any weight gain due to blocked particles with sizes greater than 0.45 μm. The membranes were found to have no apparent weight gain after filtering 5 ml of 5% solutions. In order to determine the molecular (or colloidal) sizes and distribution of these soluble materials, small amount of the filtered solutions were dissolved in THF to make a solution for GPC analysis. The GPC chromatographs are presented in figure 14. Judging from the chromatographs, it became apparent that the sizes of the eluents were too small to be viewed as colloidal particles. They were actually in the equivalent polystyrene molecular weight range of a few hundred to a few thousand. Thus the DMSO solutions had to be true solutions and the solute had to be of finite structures. The concept of microgel is therefore not applicable to the current system. Materials from B-a cured at 180°C or above for half an hour could not be completely dissolved in DMSO at the same conditions. The gelTg of the B-a system, therefore, must be higher than 170°C but lower than 180°C. Thus, at temperatures of 170°C
and below. $T_{\text{cure}}$ is lower than $gelT_g$. the curing system had not reached the chemical gelation point when they started to vitrify. Consequently, the use of Arrhenius equation for calculating the activation energy of the curing reaction for B-a system from Figure 8 would not be justified. All the dynamic and relaxation phenomena then had to be attributed to the rheological characteristics of the curing system before chemical gelation.

The phenomenon of two sets of relaxation times has been well understood and documented in the viscoelastic properties of linear polymeric materials with high molecular weight. It has been attributed to the existence of chain entanglements (18). In the relaxation spectrum of a high molecular weight polymer under very wide range of experimental frequency or time, a viscoelastic material exhibits three regions (glassy, rubbery, and viscous flow) and there are two sets of relaxation processes connecting them. The first is called transition zone existing between the glassy and rubbery regions while the second is called terminal zone existing between the rubbery and flow regions. The rubbery region is also called plateau zone whose existence is the sole consequence of physical entanglements. It is remarkable that we could witness part of the transition zone, plateau zone, and the terminal zone within four decades of time (0.01 to 120 seconds) in the above stress relaxation experiments of curing B-a. Since the plateau zone is usually quite narrow for linear polymers unless the polymer has extremely high molecular weight, and the system being studied obviously did not have very high molecular weight as shown by the GPC chromatographs in Figure 14, the effect of physical entanglements in the B-a system could not be afforded by the long length of linear chains in the classic sense, but rather by some topological and physical frictional forces among the abundant dangling branches formed as intermediates for an
eventual cross-linked network. We would like to stress the intermediate nature of the structures since similar secondary relaxations were also observed in early stages of curing at 220 and 240°C (Fig. 12 and 13). A macroscopic network could be built on such intermediate structures if the material vitrification had not hindered further reactions, as shown by the later stages of stress relaxation experiments in Figure 12 and 13. How much contribution to the frictional forces do the inter- or intra- molecular van der Walls or hydrogen bonding forces have is a question to be determined by detailed molecular analysis of the structures. However, this is beyond the scope of the current work. In total, the frictional forces are due to physical as well as topological interactions in the branched structures, and are the underlying mechanism of the above rheological behavior. The molecular structures most likely consist of highly branched structures. However, possibility of cyclic structures is not excluded.

The difference in the rheological behaviors of systems B-m and B-a certainly suggested that there had to be some differences in the molecular structures of the their corresponding intermediates. No answer could be arrived without detailed molecular analysis on the intermediate structures. However, there was some indication that the reaction paths involved in the curing of B-m and B-a might be different. It was reported previously that the electron rich aniline moiety was able to react with formaldehyde moiety under certain circumstances (19,20). Thus, the ring-opening reaction of 3-phenyl substituted 1,3-dihydrobenzoxazine in B-a might involve more than one reaction scheme. Further experiment would be desirable in understanding the structural differences.

Irrespective of the structural specifics of the curing B-a, The fact that molecules of relatively small sizes were able to generate rubbery plateau in the
viscoelastic response of the material is a very interesting rheological phenomena. There has been some evidence in the literature for additional relaxation behavior observed in the study of the viscoelastic properties of multi-branched polystyrenes whose branches had molecular weight lower than the critical entanglement value (21). This coincidence led to the consideration that there might be some relaxation behaviors characteristic of a highly branched structure which occur at molecular weights much lower than the entanglement molecular weight of a linear chain system. The understanding of rheological behaviors of branched structures which serve as an intermediate in cross-linking systems are currently very limited in the literature.

One feature which distinguishes the B-a curing system from a thermoplastic material in stress relaxation behavior and indicates its intermediate nature is the magnitude of the plateau zone moduli. For thermoplastic materials, the plateau modulus depends only on the average molecular weight between entanglement points ($M_e$) as expressed in the following simplified equation (18):

$$G_{eN} = \frac{\rho RT}{M_e}$$

where $\rho$ is the density, $G_{eN}$ is the pseudo-equilibrium modulus in the plateau region. Thus, $G_{eN}$ is independent of the molecular weight of the whole chain. The plateau zone modulus would not increase with increasing molecular weight once it is beyond the entanglement molecular weight $M_e$. In the current systems, the plateau zone moduli kept increasing as the curing reaction continued as if the $M_e$ reduced. This increase of the pseudo-equilibrium modulus $G_{eN}$ values in the plateau zones resembled the increasing cross-linking density in the development of chemical cross-links as indicated by the $G_\infty$ in the B-m system. The difference
was that the $G_e N$ at 160°C or 170°C curing eventually decayed to zero in a secondary relaxation due to the lack of chemical crosslinks. Thus the intermediate structures encountered during the curing process bear some of the characteristics of both thermoplastic and thermostet materials. The process of curing can be viewed as a process of transformation from thermoplastic to thermostet characteristics. The extension of the plateau zone also reflected the process of chemical reactions which generates increasingly branched structures, and eventually forms a chemically cross-linked structure if vitrification had not impeded its progress. This halt in the reaction due to vitrification would be overcome at higher temperatures, thereby allowing crosslinking to occur.

In considering the dynamic experiments, since the $G'$, $G''$ crossing point coincided with the emergence of the plateau zone in stress relaxation experiments, it was reasonable to assume that it might correspond to physical gelation at the experimental time domain (10Hz) whose molecular mechanism was physical interaction instead of chemical gelation. The relationship between dynamic and steady experiments for systems without an equilibrium relaxation modulus can be established by the following Fourier transformation:

$$G' (\omega) = \omega \int_{0}^{\infty} G(t) \sin (\omega t) \, dt$$
$$G'' (\omega) = \omega \int_{0}^{\infty} G(t) \cos (\omega t) \, dt$$
In the derivation of Winter et al., the effect of physical entanglement or phase separation was excluded, correctly so for purpose of simplicity. Thus, for the criteria $G'(\omega)=G''(\omega)$ (or $G''(\omega)/G'(\omega) = \text{constant}$) to be used for gelation determination, the critical relaxation modulus $G(t)$ at gelation has the form of $St^{-n}$ (11,12). Here only one set of relaxation times is involved which is adequate for probably many thermoset precursors where chemical gelations take place before other physical forces start to play profound roles. In the current investigation, the B-m system follows this behavior and the dynamic method was adequate in describing its chemical gelation behavior. But in practical application systems, it is also possible, irrespective of the curing temperatures which may be either higher or lower than the ultimate material $T_g$, that this critical condition be fulfilled without invoking chemical crosslinking. Physical entanglements and/or interactions in the system could well provide such condition. Thus, one should always be careful in applying the dynamic measurement for gelation determination. It has been shown in the above discussion that the dynamic measurement was not applicable to the B-a system. In B-a at curing temperatures of 170°C and lower, all the rheological behaviors in the previous discussion were dominated by physical forces among the highly branched intermediate structures before chemical crosslinking. The effect of intermediate structures could be realized even at high temperatures as shown in Figure 12 and 13. It is also quite noticeable that in a certain thermosetting system the effect of such topological and physical forces could be realized at relatively small molecular sizes due to frictions among the abundant number of branches. The geometric shape of the branched structures is perhaps as important.

CONCLUSIONS
The method of dynamic measurement of the formation of gel structure has been shown to be applicable to one of the two curing systems in current investigation. For the B-m system, the $G'$, $G''$ crossing point was shown to be within the gelation window determined by stress relaxation experiments. The logarithmic gel times thus determined at different temperatures were found to follow a linear relationship with reciprocal temperature, allowing the calculation of the activation energy of the curing reactions. The activation energies for curing B-m system was found to be 25 kcal/mole. For the B-a curing system, the $G'$, $G''$ crossing point was shown to correspond to phenomenon other than chemical gelation which, in this case, might be topological and physical forces among the branched chains in the intermediate structures.

Stress-relaxation experiments were shown to be a very useful technique in monitoring the structural evolution of the curing systems. The two sets of relaxations encountered in the B-a curing system at certain temperatures were suggested to be due to the formation of certain intermediate structures which could eventually be cured into continuous network structures at higher temperatures.

It is an interesting rheological phenomenon that the branched structures existing in the B-a curing system which, with relatively low molecular sizes, were able to generate rubbery plateau in the viscoelastic response of the materials. Detailed molecular structural analysis are highly desirable in determining the intermediate nature of the branched structures. This may provide insight as to the process of building the molecular architectures in crosslinking materials.
REFERENCES


13. chapter II of this thesis.

14. chapter III of this thesis.


Table 4.1. Gelation times and activation energy

<table>
<thead>
<tr>
<th>Temp.(°C)</th>
<th>B-m tgel(min)*</th>
<th>tanδ**</th>
<th>t (G'G&quot;)</th>
<th>tanδ**</th>
</tr>
</thead>
<tbody>
<tr>
<td>131</td>
<td>46</td>
<td>7.83E-1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>140</td>
<td>20.2</td>
<td>4.68E-1</td>
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<td></td>
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<tr>
<td>150</td>
<td>10.0</td>
<td>2.66E-1</td>
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<td></td>
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<tr>
<td>155</td>
<td></td>
<td>36</td>
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<tr>
<td>160</td>
<td>6.0</td>
<td>1.46E-1</td>
<td>19.8</td>
<td>6.13E-1</td>
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<td>12.8</td>
<td>4.81E-1</td>
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<td>9.16E-2</td>
<td>9.2</td>
<td>3.23E-1</td>
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<td>7.8</td>
<td>2.48E-1</td>
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<tr>
<td>Ea(kcal/mole)</td>
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<td></td>
</tr>
<tr>
<td>r(cors coef.)</td>
<td>1.00</td>
<td></td>
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</tr>
</tbody>
</table>

* at G'=G" in isothermal curing, 10 Hz freq
** lowest value before vitrification
Figure 4.1 Dynamic viscosity evolution during isothermal curing of B-m
Figure 4.2
B-m isothermal curing at 140°C
Figure 4.3
B-m Isothermal curing at 150°C

\[ \tan \delta \]

\[ G, G' \] (Pa)

Time (min.)
Figure 4.4  Arrhenius plot of B-m gel time

\[ E_a = 2.5 \text{ kcal/mole} \]
Figure 4.5  Equilibrium $\tan \delta$ at different curing temperatures
Figure 4.6  Dynamic viscosity evolution during isothermal curing of B-a
Figure 4.8
Arrhenius plot of B-a $G', G''$ crossing time

$\log t (G''=G')$

$\frac{1000}{T}$

Values: 2.0, 1.5, 1.0
Figure 4.9  Stress relaxation moduli $G(t)$ for B-m isothermal curing
at 150°C
(starting time of the curves from bottom up: 6, 9, 12, 15, 18, 21 min.)
Figure 4.10 Stress relaxation moduli $G(t)$ for B-a isothermal curing at $160^\circ$C.

(Starting time of the curves from bottom up: 15, 18, 21, 24, 27, 30 min.)
Figure 4.11  Stress relaxation moduli $G(t)$ for B-a isothermal curing at 170°C
(starting time of the curves from bottom up: 5, 8, 11, 14, 17 min.)
Figure 4.12 Stress relaxation moduli $G(t)$ for B-a isothermal curing at 220°C
(starling time of the curves from bottom up: 9, 13, 21, 31, 51 min.)
Figure 4.13
Stress relaxation moduli $G(t)$ for B-a isothermal curing at 240°C
(starting time of the curves from bottom up: 5, 9, 13, 18 min.)
Figure 4.14  GPC chromatographs of B-a cured at 160°C and 170°C.
PART 2

RIM-PULTRUSION AND MATERIAL CHARACTERISTICS

OF

NYLON-6 AND RUBBER-TOUGHENED NYLON-6
Chapter V

RIM-PULTRUSION OF NYLON-6
AND RUBBER TOUGHENED NYLON-6 COMPOSITES
INTRODUCTION

There has been strong interest in the research and developments of thermoplastic composites in recent years. As matrix materials in structural composite applications, the thermoplastic materials have many advantages over their thermoset counterparts because of their inherent toughness. The fabrication of thermoplastic composites, however, requires high temperature for melting and forming. Another major difficulty is the achievement of good wetting of the reinforcing fibers due to the high viscosity of the polymer melt. The RIM-Pultrusion is a new and unique process for fabrication of continuously reinforced composites which was first developed in this laboratory (1). Technically it combines the advantages of both the reaction injection molding (RIM) and the pultrusion processes while avoiding their inherent shortcomings. The conjunction of RIM and pultrusion makes RIM a continuous process, instead of a batch process, and at the same time eliminates the use of a resin tank in the pultrusion operation. This technique applies to both thermoplastic and thermoset materials so long as they have an adequate reactive chemistry to be RIMable. The low viscosity of the reactive precursors also enables excellent fiber wet-out and fiber-matrix adhesion. In this chapter, the preparation of unidirectionally reinforced nylon-6 and rubber-toughened nylon-6 composites is described. The toughening rubber domains emerged during the course of polymerization and/or solidification as a result of the chemistry employed. The material characteristics of the composites are discussed in terms of morphology and dynamic mechanical properties.

EXPERIMENTAL
The design of the RIM-Pultrusion process and the machinery have been described in detail elsewhere (1). The two streams of chemicals for RIM contained initiator and catalyst respectively. The catalyst used in this research was sodium caprolactam prepared by reacting anhydrous caprolactam with sodium hydride. The initiators were hexamethylenediisocyanate or diisocyanate terminated polypropyleneoxide with a number average molecular weight of 4,000 and polydispersity of 2.1 (by GPC). The caprolactam was supplied by the Allied Signal company and vacuum dried at 60°C for 24 hours before use. The polymeric initiating species was prepared by reacting anhydrous dihydroxy-terminated polypropylene glycol (mw=2,000, from Fluka) with 1.5 molar equivalent of hexamethylenediisocyanate (from Aldrich) at 100°C. This RIM system has a slight difference from a commercial nylon-6 RIM system developed by Monsanto in the detailed structures of the initiating and catalyzing species. Composites made with 10, 15, and 20 wt% rubber contents in the matrices are designated in this chapter as NY10, NY15, and NY20 respectively. The concentrations of initiator and catalyst were both 0.75% based on molar functionality. During the RIM-Pultrusion operation the chemicals were maintained at 100°C in the reservoirs that contained the chemicals as well as at the mixing head and the resin impregnation chamber where the individual filaments were wetted by the low viscosity chemicals. The pultrusion die was 91 cm (36 inch) long and had a circular profile of 0.935 cm (3/8 inch) diameter. The fiber content of the composite was controlled by the number of the glass fiber rovings pulled through the die. In a typical case of 45 rovings, the fiber content was 72±1 wt% as determined by ashing segments of the composite rod produced. This corresponds to about 50 vol% of the final composite. This fiber content was chosen for the ease of studying the composite relaxation behavior.
which is matrix dominated. The process itself is capable of handling even higher fiber loading.

Several process parameters were involved to affect the quality of the pultruded product. The first parameter is the die temperature profile which directly influences the heat transfer to the resin and thus the curing process. The profile was designed to accommodate the requirements of heat transfer in the first zone, gelation in the second zone and final cooling in the exit zone. The second parameter would be the pulling speed which determines the resin residence time in the die as well as the pulling force. This was chosen in conjunction with the die temperature profile to ensure complete curing. A pulling speed of 40.6 cm/min (16"/min) was chosen for a temperature profile of 140°C-160°C-150°C in this study. Another parameter associated with the process is the ratio of the amount of resin injected from the RIM mixing head against that incorporated into the final formed composite. A ratio greater than 1 is required for the semi-continuous pultrusion without resin deficiency. In current case with a computerized step-motor mini RIM machine, a ratio of 1.3 was maintained.

The samples for mechanical relaxation studies were rectangular bars typically of dimensions 60x8x2.5 mm. These samples were obtained by sanding the cylindrical composites into rectangular shapes of desired dimensions. A Rheometrics RMS-800 dynamic mechanical spectrometer was used to study the mechanical relaxation properties of the composites. Transverse shear deformations were applied. The 0.04% strain was chosen so that it was well within the materials' linear viscoelasticity regime as determined by a strain sweep experiment while providing a reasonable torque response. Sample thermal equilibrium was
assured by allowing one minute of thermal soak time before starting measurements at each temperature.

A JOEL JSM-35CF scanning electron microscope (SEM) was used to observe the morphological features of the composites. The fracture surfaces of the composites were obtained by failing the composite samples in the Izod impact tests.

RESULTS AND DISCUSSIONS

Figure 1 illustrates the measured static temperature profile of the die under the 140°C-160°C-150°C heater cartridge arrangement. The actual temperature profiles during the pultrusion operations would also depend on the resin formulation, the pulling speed as well as the entry temperatures of the components (resins and fibers). Positive pressure was achieved at the first zone due to thermal expansion of the resin precursor materials which were subjected to heat transfer from the die and the exothermic heat generation from the polymerization reaction (2). The low initial viscosity and the positive pressure helped complete wet-out of the fiber filaments. It was found that composite produced had a nearly zero void content by SEM examinations.

Fourier Transform Infrared spectroscopy has been proven a powerful technique to monitor fast changes on the molecular level. The nylon-6 RIM reaction is finished in 52 seconds at 160°C as determined by FT-IR study (3). Figure 2 shows FT-IR kinetics spectra of NY20 at the frequency range of 1500 cm\(^{-1}\) to 1720 cm\(^{-1}\); showing the appearance of the linear amide II band (at 1544 cm\(^{-1}\)) of nylon structure and the transformation of the lactam carbonyl band (at 1671 cm\(^{-1}\)) into the linear amide I band (at 1643 cm\(^{-1}\)) during polymerization as modeled at 140°C (band assignment is refereed to ref.3). The crystallization also
occurs and develops during the polymerization. In current thermoplastic system, the gelation starts when the crystallization or phase separation occurs. This could happen when the propagating chains reached a certain molecular weight. In Figure 3 the polymerization of the resin was monitored by a dynamic mechanical spectrometer (rheometer) using a 25mm diameter parallel plate geometry. The storage modulus, $G'$, and the loss modulus, $G''$, were shown together with the dynamic viscosity, $\eta^*$, curve as a function of reaction time at 130°C. It should be stated that Figure 3 does not represent isothermal process since the temperature of a 1 mm thick sample would not be uniform within the reaction time due to poor heat transfer and exothermic nature of the reaction. However, the temperature would not exceed 135°C under these conditions. At the beginning, the $G''$ was higher than $G'$, indicating the fluidity of the system with the viscosity around 10 centipoise. It is at this stage the resin impregnation was achieved. As the structure built up during the polymerization, the elasticity of the system increased so that the $G'$ eventually surpassed $G''$. The crossing point is taken as an indication of the gel point which, in this case, occurred at a viscosity of around one hundred poise. During the pultrusion operation the chemicals had about two minutes' residence time within the die at the pulling speed of 40 cm/min. This would allow the resin solidification in the central stage of the die at the temperature profile indicated in Figure 1. The physical nature of gelation might correspond to crystallization for pure nylon-6 and either crystallization or phase separation, or more likely a combination of those two processes for rubber-toughened matrices. After solidification, further molecular weight and structural built-up are possible in the solid state (4).

Viscoelastic Properties of the Composites
The mechanical relaxation behavior of the composite is very sensitive to the processing conditions. An incomplete polymerization might still provide a composite rod with good appearance and reasonable integrity, but the dynamic mechanical behavior would be quite different from that of a well polymerized sample. A much lower position of the $\alpha$ transition would be one experimental result. Thus it can be a sensitive monitor for quality control. Another important factor in determining the dynamic relaxation spectrum is the thermal history of the sample. Thus the original pultruded sample will exhibit certain differences in the spectra after it was subjected to heat treatment. Figure 4 shows the relaxation spectrum of nylon-6 in the temperature range of -140°C and 180°C. The $\alpha$ relaxation at 76°C represents the breakup of hydrogen bonded nylon chains in the amorphous region. The $\beta$ relaxation at -82°C has been linked with the movement of amide containing chain segments in the nylon amorphous region(5,6). Figure 5 is the dynamic mechanical spectra of nylon composites before and after annealing at 85°C in vacuum for 40 hours. It can be seen that the relaxation behavior was, as expected, essentially the same as that of the pure matrix materials. In next chapter, studies on the mechanical relaxation behaviors of RIM nylon-6 will be described. This study indicates that the shift of the $\alpha$ relaxation in Figure 5 was the result of structural changes caused by annealing which corresponded to the increase in crystallinity due to formation of small nuclei in the amorphous region. The newly formed nuclei function as crosslinks to restrain the chain motions in the hydrogen bonded amorphous region.

The fact that we were able to obtain $T_g$ around the expected temperature of nylon-6 glass transition indicates that the polymerization was essentially complete in the RIM-Pultrusion operations.
It is noteworthy that in the presence of about 50 vol% glass fiber; the α transition in the composite occurred at a temperature higher than that of a pure nylon-6 and was more diffuse. It should be pointed out that the glass fiber has no transition in the temperature range studied. Furthermore the transverse shear deformation applied to the composite sample was more sensitive to the matrix and the fiber-matrix interphase. The upshift of the α transition and its diffuseness could be viewed as the existence of more restricted motion of amorphous nylon chains by enhanced bonding with the fiber.

This indicates good adhesion between fiber and matrix. Since the glass rovings came with an amide compatible sizing agent, and the filaments were completely wet out by the low viscosity molten caprolactam, good bonding was expected in the composite.

In cases of the polypropyleneoxide-nylon copolymers, the precursors had slightly higher viscosity but were still low enough (about 10 centipoise) at mixing and impregnation temperature of 100°C to ensure good fiber wet-out. The chemistry of the curing was the same as the pure nylon RIM except that an additional physical process, phase separation, was introduced to the system. Figure 6 shows the annealing effect on the relaxation behavior of NY20 where 20 wt% of the matrix material was the rubbery polypropyleneoxide segments in a block copolymer form. The existence of the rubber glass transition at -70°C was distinct and did not change its shape or position after annealing. The lower α peak position of the original composite indicates lower order of hydrogen bonding structure in the amorphous region of nylon-6. The shifting of the nylon α peak upon annealing, therefore, was much more dramatic than in the case of the pure nylon composite. Thus the original states of the nylon and rubber-toughened nylon
composites running off the process were different in term of physical structures. This was probably due to the differences in the thermal conductivity of the nylon and toughened nylon systems. Other influencing factors might be the phase separation and possible preferential deposition of nylon or rubber domains onto the fiber filaments. As a result of the fast kinetic nature of the RIM process, the phase separation was expected to be incomplete. Thus some fraction of the rubbbery segments would remain in the nylon amorphous phase when the gelation occurs which might decrease the affinity among the nylon chains. This process was much more complex than in the case of pure nylon composite. The direct reflection on the mechanical relaxation spectra was that the annealing not only serves to enhance the degree of hydrogen-bonding in the amorphous structures, and produce restraints in the nylon amorphous region by forming small nuclei (4), but also serves to increase the degree of phase separation and to relax the thermal stresses in the composite induced during the processing. In accord with this, the α transitions were more diffuse than in the case of nylon-6 composite, especially for the unannealed original sample. After annealing, however, the α transition still occurred at slightly higher temperature than NY20 matrix, indicating that the chemical reaction was complete after the RIM-Pultrusion operation even although the physical state of the composites was far from equilibrium.

Electron Microscopy of Fractured Surfaces

Figure 7 is the scanning electron microscope (SEM) picture of the fractured surface of the nylon-6 composite. The fracture was achieved in a specimen subjected to unnotched Izod test where load was applied transverse to the fiber alignment direction. Excellent fiber-matrix adhesion was exhibited in this figure as the fiber and the resin essentially formed an integrated entity and no debonding was
observed upon failure. Note that the individual filaments were completely wet and the void content was nearly zero. This excellent integrity and interface bonding ensured the complete transfer of stress loading to each filament. However, the lack of damping mechanisms in the matrix as well as in the interface at room temperature also caused complete breakage of the composite upon failure in the Izod tests where the load was applied in the transverse direction, though a nylon composite is believed to have higher toughness in comparison with other matrices. The failure behavior of the rubber toughened composites towards transverse loading, however, was different from that of the nylon composite. Instead of complete breakage of both the fiber and the matrix for nylon-6 composite, the toughened composites showed minor fiber damage due to yielding of the softer matrices. Figure 8a is the SEM micrograph of the NY10 composite fractured surface. Good fiber wet-out was achieved irrespective of the higher viscosity of the precursor. As can be seen from the SEM micrograph in Figure 8b for NY20 composite fractured surface, the interface bonding was weaker than in the case of pure nylon composite, and delamination was seen as the major cause of failure. The channels left over by fiber pullout was clearly visible in Figure 8b. The existence of small rubber domains (submicron in this case, and was unreveable to the SEM) would probably have initiated cavitation or debonding in the matrix region upon impact, thus reduced the stress directly applied to the fibers. The fiber pullout also would have contributed to a higher energy absorption. Although the role of modified matrix in the toughened composite is of great interest (8); the complete analysis of the composite fracture behavior and mechanism is beyond the scope of this study.

Because of the thermoplastic character of nylon-6 and rubber toughened nylon-6, the composites obtained from the RIM-Pultrusion operations can be easily
postformed at elevated temperatures. Compression molding of the pultruded rods was demonstrated with press temperature at 250°C and 1.4 MPa pressure. The molded specimen exhibited higher shear modulus in the dynamic test than the original pultruded specimen as shown in Figure 9. This is primarily because of the fact that there was much less fiber damage at the specimen surface as compared with the specimens from the pultruded rods which were sanded down to required dimensions. This compression molding process also served to relax the thermal stresses induced during the RIM-Pultrusion operation. Furthermore, no fiber damage in the composite was witnessed since they were very well protected by the surrounding matrix resin and, of course, with inherently low shear rate of the compression molding process.

CONCLUSION

The RIM-Pultrusion process has been successfully applied to prepare unidirectionally reinforced composites of nylon-6 and rubber toughened nylon-6. The composites exhibited excellent wetting and mechanical integrity due to the low viscosity of the precursors used in the process.

The dynamic mechanical properties of the nylon-6 and rubber toughened nylon-6 composites have been shown to resemble that of the corresponding matrix materials. The slightly higher \( \alpha \) transition temperatures and diffusiveness of the transitions were believed to be the result of fiber introduced restraints on the molecular motions and inhomogeneity as compared with the matrices. The possibility of engineering the composite impact failure behaviors by using rubber toughened matrices to achieve a higher toughness was illustrated.
REFERENCES


7. chapter VI of this thesis.

Figure 5.1  Pultrusion die temperature profile
Figure 5.2
FTIR spectra of NY20 RIM process at 140°C
Figure 5.3
NY20 curing curves (nonisothermal)

F = 100 rad/s
Dynamic mechanical spectra of nylon-6 composites

Figure 5.5

(△ original, ○ annealed)
Figure 5.6
Dynamic mechanical spectra of NY20 composites
(Δ original, O annealed)
Figure 5.7  SEM photograph of the fracture surface of nylon-6 composite
Figure 5.8  SEM photograph of the fracture surfaces of a). NY10, and b). NY20 composites
Figure 5.9 Dynamic mechanical spectrum of compression molded RIM-Pultruded nylon composite
Chapter VI

DYNAMIC MECHANICAL ANALYSIS OF RIM NYLON-6
INTRODUCTION

Reaction injection molding is a process which allows the formation of polymeric products in-situ, within the mold, from monomeric or oligomeric precursors. This is a rapidly growing industry owing to its high productivity and inexpensive capital equipment requirements (1,2). To date, the polyurethane RIM system has been the most versatile and widely used RIM material with applications ranging from automobile fascia and seating to business machine housings. RIM nylon-6 and rubber toughened nylon-6 systems have also been developed. There have been extensive efforts to develop new RIM systems for specific applications. Polyurea, polyacrylamate, epoxies, and polycyclicpentadiene have already reached various levels of practical applications. Among these systems, nylon-6 and modified nylon-6 are thermoplastic and have long been recognized as excellent engineering materials which offer mechanical properties difficult to match by other RIM systems. Their thermoplastic character also enables RIM produced parts to be post-formed, which greatly enhances design and process flexibility.

Since it is a widely used engineering material, the mechanical, viscoelastic, spectroscopic and other properties of nylon-6 have been extensively studied over the past years. Those studies have provided much insight into the material structure and behavior. However, there are still some unanswered questions, especially in the area of viscoelastic relaxation behavior. For RIM nylon-6, only a few studies have been reported so far, but even these have revealed certain characteristic structural features which distinguish it from conventionally processed nylon-6 materials. These features simplify the structural complexity normally found in the non-RIM materials and may provide an avenue to solve some of the problems associated with the understanding of conventional nylon-6. It was reported that
unlike conventional nylon-6 materials produced from injection or compression molding processes. RIM nylon-6 contains entirely monoclinic or α phase crystalline structure. The crystallinity is higher and the average size of the spherulites is small as compared with injection molded counterparts (3). This provides a better defined background to evaluate other factors influencing the viscoelastic properties of the material, and thus would be an ideal system to clarify some of the uncertainties researchers have encountered in the past, such as the influence of moisture and the very existence of the β relaxation process.

**EXPERIMENTAL**

The anionic polymerization of caprolactam is the basis for current RIM nylon-6 practices. Two streams of chemicals were prepared in the experiments, one consisting of a base catalyst dissolved in caprolactam and the other of an acyl-lactam initiator in caprolactam. The two streams of molten caprolactam were mixed in an impingement device and injected into a heated mold where the mixture polymerized and solidified into final part. The chemical systems used in this work are illustrated in Figure 1.

The caprolactam was purchased from Aldrich and dried by distilling off 10% of the original content under vacuum. Other chemicals were also purchased from Aldrich and used without further purification. The overall molar concentrations of both the catalyst and initiator were 0.75%. The chemicals were mixed at 100°C and the polymerization took place at 160°C. All preparations were performed in either a glove box or a glove bag purged with dry argon gas. The mold which made samples for dynamic mechanical measurement was an open mold assembled mechanically with a glass slide and stainless steel bars. No mold release
agent, nor adhesive, was used. The samples were allowed to cure at 160°C for three minutes, slightly longer than commercial RIM operations in consideration of the heat transfer factor in the mold. They were then cooled in a P₂O₅ desiccator and sanded down to desired dimensions (typically 55x10x2.5mm).

A Rheometrics RMS-800 dynamic mechanical spectrometer was used for the viscoelastic studies. The instrument was equipped with a force rebalance transducer and an air convection oven with temperature control capability from -150°C to 600°C with deviation no larger than 1°C. The rectangular samples were subjected to transverse shear deformation. The strain magnitude was kept at 0.04% for all experiments. This was chosen to give an adequate torque response and was well within the regime of material linear viscoelasticity. A temperature/frequency ramp mode was designed so that measurements were carried out at each temperature for four frequencies throughout the -140°C to 180°C range. In order to assure thermal equilibrium in the sample during measurements, a one minute thermal soak time was maintained after reaching each new temperature before starting to collect data.

X-ray diffraction data were obtained in a Philips APD3520 diffractometer. The sample holder was specially designed so that the same specimen used in the mechanical relaxation study could be placed into the scattering chamber of the X-ray diffraction instrument. This would enable direct correlation between the mechanical relaxation properties and the sample crystallinity.

RESULTS AND DISCUSSIONS

β Transitions of RIM Nylon-6
There have been extensive studies of the mechanical relaxations of polyamides in the past few decades for which good review articles are available (4.5). Essentially, there are three relaxation processes in the temperature range -160°C to 200°C, namely the α, β and γ transitions occurring at around 70°C, -40°C and -140°C, respectively, for an experimental frequency of 100Hz (6). The molecular mechanisms of these relaxations have been widely discussed, but unanimous agreement has not been reached, especially for the β and γ transitions. It is believed that the α process involves the rupture of hydrogen bonds between chains in the amorphous region (7). The β process involves the motion of chain segments, including the amide groups, which may be associated with water molecules (8). The crank-shaft motion mechanism of methylene sequences was proposed for the γ process which occurs at almost the same temperature as that of polyethylene, but dielectric relaxation also suggested motions involving polar groups (9).

The water content of the sample significantly affects all three of these relaxation processes. Moisture was believed to play the role of plasticizer, enhancing the mobility of the chains which are otherwise held together by hydrogen bonding. This is achieved by the water molecules forming hydrogen bonds with the amide groups on the chains. The loss maximum of each relaxation process shifts to lower temperature as the concentration of water increases (8). The magnitude of the transition is also affected by water content. This holds true for all three processes, but to a much greater extent for the β and γ processes. It was reported for nylon-612, nylon-610 and nylon-66 that the β peaks were nearly eliminated by drying operations (4). The magnitude of the β relaxation for nylon-6 was also reduced significantly by drying the oriented sample specimen; however,
for isotropic samples the \( \beta \) relaxation peak remains, irrespective of the drying operation (8). In some reports, even though the author claimed disappearance of the \( \beta \) relaxation after drying, the actual plot still showed the existence of a shoulder. Overall, there has been no experiment which could attribute the \( \beta \) relaxation solely to the chain-water complex mechanism, nor has there been any work which isolates the contributions to the \( \beta \) relaxation from water and from mechanisms not associated with water. Taking advantage of recent advances in instrumentation for mechanical spectroscopy, and understanding of the structural features associated with reaction injection molding; the current work hopes to illuminate these separate contributions in nylon-6.

Figure 2 is an X-ray diffraction pattern of the RIM nylon-6. It illustrates the simplicity of the crystalline structure. Only the monoclinic \( \alpha \) crystalline structure was observed. Although all three relaxation processes discussed here are believed to occur in the amorphous region, the establishment of a single crystalline phase simplifies further discussion.

The practice of drying reported in the literature usually involved vacuum at elevated temperatures, sometimes as high as 150°C. This process was probably necessary for commercially supplied samples used in previous reports, however, it inevitably caused annealing which would change the morphology and crystalline structures of the original samples. The subsequent chain organization in the amorphous region and the hydrogen bonding structures between the chains would be highly dependent on the specifics of conditioning. In order to avoid this unintentional annealing effect and take advantage of the RIM process, the current samples were prepared with extreme caution in the operations. The process started with dry caprolactam monomer and the reaction was performed under a dry argon
atmosphere so that the as-prepared sample would be nearly moisture-free. Figure 3 is a temperature sweep for this sample at a frequency of 10 radian per second (1.6 Hz). The shear storage modulus G' and loss modulus G" are plotted on a logarithmic scale. The α transition occurs at 59°C at this frequency. The β relaxation appears to be a shoulder on the much more intense γ peak, and the peak temperature of the β process is approximately -86°C. Further drying in vacuum at 40°C for 72 hours resulted in neither weight loss nor change in the position and magnitude of the dynamic mechanical spectrum. Thus, such a sample should be representative of the dry, original RIM nylon-6.

The effect of water on the relaxation spectra has been reported in many previous studies (4,7). It has been established that the moisture absorption by nylon-6 shows a break point around 1-2 wt% (10). In terms of molecular interaction between the water molecules and the polyamide chains, it indicated that there are tightly bound water molecules forming hydrogen bonds directly with the chain amide groups before the break point and loosely associated water molecules absorbed after the break point. The moisture content probed in this presentation would fall in the first category and below 1wt%.

Controlled moisture uptake of an original sample was achieved by placing an open vial containing the sample in a jar with water at the bottom for a specified time. The sample was then equilibrated at 40°C for 96 hours in a sealed vial and was then weighed to determine the moisture content. Figure 4 shows temperature sweeps of the dynamic mechanical spectra of nylon-6 samples containing 0.4 wt% (triangles) and 0.1wt% (pentagons) moisture levels at a frequency of 10 rad/sec. The existence of β peaks at -71°C and -60°C is clearly visible. They are much more intense than the β peak in the original sample and occurred at higher
temperatures. When the moisture content was reduced from 0.4% to 0.1%, the position of the β peak maxima shifted to higher temperature and at the same time the magnitude decreased. For a sample specimen with even lower moisture content, we would expect a β-peak temperature above -60°C or complete disappearance. In Figure 5 the G'' spectra of samples with 0.4, 0.1, 0.07 wt% moisture are plotted together with the spectrum of the original dry sample. The peak maximum of the sample with 0.07 wt% moisture content at the β range occurs at -58°C, slightly higher than that of the 0.1 wt% moisture content sample. Since no peak was detectable above -58°C in the original sample, it was reasonable to propose that the moisture effect was minimized in this sample, and therefore the peak at -86°C must have mechanism not associated with moisture. We would label the relaxation at higher temperature, which is apparently water-related, β₁ and the other peak occurring in the original dry sample, β₂ in this context.

If these two peaks in dry and wet samples indeed correspond to different mechanisms, a difference in their activation energies would be expected. Figure 6 is a plot of logω versus 1/T where T is the peak temperature of the transition at frequency ω in the G'' spectra of the 0.4% moisture content sample and the original dry sample. The activation energies were found to be 14 kcal/mole and 10 kcal/mole for the β₁ and β₂ processes, respectively. A Similar plot could also be constructed from the tanδ spectra with activation energies of 16 kcal/mole and 11 kcal/mole respectively. The error of the activation energy measurements was estimated to be no larger than ±1.0 kcal/mole by parallel experiments. Furthermore, if these two processes can occur simultaneously in bulk nylon-6, it should be possible to observe and differentiate them simultaneously in a mechanical spectrum. By careful selection of moisture level and use of a low dynamic
operating frequency, this was indeed achieved. Shown in Figure 7 are the $G''$ spectra of the sample with 0.07 wt% moisture content obtained across three decades of experimental frequency. At 0.1 rad/sec, the two peaks were clearly discernible and occurred at -94°C and -112°C respectively.

Previous investigations had reported activation energy values for the $\beta$ process at 13-17 kcal/mole (11). It becomes clear that these values correspond to the $\beta_1$ process, which is definitely associated with water. This assessment will be further substantiated by activation energy data discussed below. As to the origin of the $\beta_2$ relaxation, it might be due to the existence of residual caprolactam monomer after the polymerization since it is known that there is about 2% equilibrium monomer concentration at the polymerization temperature of 160°C (12). It has been previously reported that small amide molecules gave rise to a damping peak around the same temperature range as water (13). Considering this possibility, caprolactam-free nylon-6 was prepared by reprecipitating the formic acid solution of RIM nylon-6 into acetone. This operation would also remove the low molecular weight oligomers or cyclomers which were soluble in acetone. The dried nylon-6 was then molded. The molding process was as follows: the dry powder was first melted at 250°C under vacuum, then released to atmospheric pressure by an argon purge, and cooled down to ambient temperature. X-ray diffraction of the molded specimen showed a pattern very similar to that of RIM nylon-6 specimen, namely only reflections characteristic of the $\alpha$ crystalline structure. Figure 8 is the dynamic mechanical spectrum of this sample at 10 rad/sec. The shape of $G''$ remains the same as that of the $\beta_2$ relaxation—a shoulder on the more intense $\gamma$ transition, but the peak position occurs at -72°C instead of -86°C in the original sample. However, when we examined the frequency dependence of this relaxation, the activation
energy was found to be 11 kcal/mole. This value agrees well with the 10 kcal/mole value of the $\beta_2$ process to within the experimental error. Thus, it was believed to have the same nature as the $\beta_2$ process in the original sample. The shift in the peak position might have been caused by the morphological differences between the RIM sample and the melt crystallized sample.

Loss spectra of previous investigations repeatedly showed similar shoulder features which could not be eliminated by drying, and which were sometimes suppressed graphically by plotting $G''$ or $\tan\delta$ on a linear scale. From the current work, it seems certain that there still are relaxations active in the temperature range between the $\gamma$ and $\alpha$ transitions after excluding the effects of moisture and caprolactam. Moreover, the contribution to the shoulder of the $G''$ spectrum in the $\beta$ relaxation range, should curve resolving procedures be applied, was quite substantial. Obviously these molecular motions could be influenced by the existence of water or other small molecules. In fact, they were overwhelmed by the effect of water when it was present. But in the absence of these effects, there are still distinctive molecular motions which cannot be discarded and should rather be designated as a distinctive $\beta_2$ process. Considering that dielectric analysis also showed relaxation activity in the $\beta$ temperature region after drying (9), it is reasonable to suggest that the amide groups are involved in motions of chain segments which are independent of the presence of water.

**Effect of Moisture and Annealing on the $\beta_1$ and $\alpha$ Processes**

An understanding of the effect of moisture on the activation energies of the relaxation processes has been lacking in the past. Once the nature of the $\beta$ relaxations is clarified, the effect of low moisture content on the peak positions and activation energies (thus the corresponding molecular motions) of the $\beta_1$ and $\alpha$
relaxation processes can be evaluated. It was, however, experimentally impossible to evaluate the $\beta_2$ relaxation process in the presence of water. Again the discussion would be limited to a range of very low moisture contents which, we believe, provides better insight into the molecular motions for each of the relaxations. Figure 9 is a $\log \omega$ versus $1/T$ plot for the $\beta_1$ process at moisture contents of 0.4, 0.1, 0.07 wt%. The plot is constructed from the frequency dependence of $G''$ spectra. Figure 10 shows the activation energies together with the peak maxima temperatures at a frequency of 10 rad/sec as a function of water content for the $\beta_1$ process. It was noticeable that, as the water content reduces, the peak maxima shifts to higher temperatures and at the same time the activation energy of the process increases from 14 kcal/mole for 0.4% water to 16 kcal/mole for 0.1% water, and to 17 kcal/mole for 0.07% water content. This is indicative of the strength of the water-amide hydrogen bonding which becomes stronger at lower water content.

The mechanism widely accepted for the nylon $\alpha$ transition is the rupture of hydrogen bonds between the polyamide chains. The hydrogen bonds are formed between the amide C=O groups in one chain and the amide N-H groups in a neighboring chain (or chains). It has long been proposed that the amorphous state in nylon materials is quite different from the isotropic random coil assembly of the conventional glassy state. Instead, a certain local order is present due to the fact that hydrogen bonding interactions require some conformational order or registry in the arrangement of neighboring chains. A mesomorphic model was believed to best describe the local order in the amorphous state (14). At the $\alpha$ transition, molecular thermal motions force the dissociation of this interchain hydrogen bonding structure which corresponds macroscopically to the loss peak at this temperature. The more
highly ordered this local structure is, the higher the temperature will be required to initiate the dissociation. Thus by forming hydrogen bonds with chain amide carbonyl groups, water molecules interrupt and deteriorate the interchain cohesive forces in the nylon amorphous state and enhance the chain mobility in the mesomorphic state.

As shown in Figure 4, the shift of the $\alpha$ peak maxima to a lower temperature for 0.4% water content sample was quite dramatic ($15^\circ C$ in comparison with the original sample), however, it was consistent with a previous study which showed $30^\circ C$ shift to lower temperature upon absorption of 1 wt% water (11). For samples with 0.1 wt% and lower moisture content, the $\alpha$ peak positions were almost the same as for the dry sample, even though the spectra at the $\beta$ range were completely different. Figure 11 is a log $\omega$ versus $1/T$ plot for the $\alpha$ relaxation at different moisture levels. The peak maxima temperatures at 10 rad/sec as well as activation energies calculated from Figure 11 are plotted in Figure 12 as a function of moisture content. It seems that the activation energy of the $\alpha$ relaxation is much more sensitive to the change of chain mobility due to water molecules than the peak temperature in the $G''$ spectrum. The activation energy increased from 61 kcal/mole for 0.4% water to 79 kcal/mole for 0.1% water and further to 95 kcal/mole for 0.07% water content. The original, dry sample has an activation energy of 97 kcal/mole and the melt crystallized sample from the reprecipitation experiment 104 kcal/mole. It must be stated that the error in the activation energy ($\Delta E_a$) determination is greater in the $\alpha$ transition region than in the $\beta$ region, and is estimated to be about $\pm 5$ kcal/mole.

Table 1 summarizes the effect of moisture on the transition temperatures and activation energies of $\alpha$ and $\beta$ processes. Also included are the transition
temperature and activation energy for a sample annealed at 85°C for 40 hours in vacuum. The purpose of annealing at relatively low temperature, just above the glass transition of nylon-6, was to observe its influence on the hydrogen bonding structure in the amorphous state, where association and dissociation of hydrogen bonded structures are thermally activated.

The effect of annealing on the dynamic mechanical spectra is illustrated in Figure 13 where the spectra $G'$, $G''$ are plotted for a sample before and after annealing treatment. The measurement frequency was 10 rad/sec. It can be seen that while the $\beta$ relaxation does not noticeably change upon annealing, the $\alpha$ peak maximum shifts to higher temperature and at the same time its magnitude decreases slightly. Investigation of its frequency dependence reveals that the activation energy does not change appreciably.

It is known that the crystallization of nylon-6 takes place at the annealing temperature used in this study (15). X-ray diffraction of the annealed sample specimen also showed that this was indeed the case under our experimental conditions. In order to observe the subtle difference in crystallinity, a subtraction spectrum of the diffraction patterns before and after the annealing treatment is shown in Figure 14. The positive subtraction spectrum through the range of diffraction angles indicated that the crystallinity was higher and the band-width at half-height (BWHH) was larger for the annealed sample.

The crystallization process is known to consist of two sub-processes, namely nucleation and growth which in combination determine the overall crystallization rate. It is believed that 85°C is a temperature which is lower than the temperatures of maximum rate of either nucleation or growth. Since it is higher than nylon-6 Tg, crystallization does occur with homogeneous nucleation playing a
greater role than subsequent growth from existing crystallites. This is in agreement with the observed changes in X-ray diffractions discussed above. These small nuclei would be formed through rearrangement of the chains to gain packing registry once the dissociation of the hydrogen bonded structures in the mesomorphic state was thermally possible. The average crystallite size after annealing, however, was reduced due to the newly formed small nuclei. Coincidentally the reduction of the area underneath the $\alpha$ process, as shown in Figure 13, indicated that there was a smaller number of chains involved in the amorphous glass transition after annealing. In other words, the formation of the nuclei came at the expense of the hydrogen-bonded mesomorphic chains. The annealing at 85°C was thus the process where some of those hydrogen-bonded chains in the locally ordered mesomorphic state dissociated to form three dimensionally ordered nuclei with a new registry of hydrogen bonding structures. The emergence of those nuclei was the direct cause of the shift of the $\alpha$ transition temperature from 59°C to 65°C. However, the fact that the activation energy does not change after annealing indicated that the chain mobility in the mesomorphic region remained the same, or at least the mobility of a certain number (15 monomeric units as indicated by Boyd (16)) of consecutive atoms involved in the $\alpha$ relaxation did not seem to be hindered by the emergence of new nuclei after annealing.

CONCLUSIONS

The contribution of absorbed water to the nylon-6 $\beta$ relaxation has been separated from other factors and identified as $\beta_1$. In the absence of water, it is shown that there is still a substantial contribution to relaxation in this temperature
range. This process has a lower activation energy than that of the chain-water complex and is identified as the structural contribution $\beta_2$, which might be the related to the motion of amide-containing chain segments. The association of water with the nylon-6 chains has been shown to depend on moisture content. The association becomes stronger as the moisture content is reduced. The association between the nylon-6 chains in the amorphous state (hydrogen bonding structures), as indicated in the $\alpha$ relaxation process, is also greatly influenced by the presence of water. The chain-chain associations become stronger as the moisture content is reduced. The annealing process at 85°C is shown to allow the transformation of hydrogen-bonded structures in mesomorphic order to a new registry in three dimensionally ordered nuclei.
REFERENCES


Table 6.1. Influence of moisture on Nylon-6 relaxation parameters
(frequency 1Hz, $\Delta E_a$ in kcal/mole)

<table>
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<tr>
<th>Samples</th>
<th>$\alpha$ Temp°C</th>
<th>$\Delta E_a$</th>
<th>$\beta_1$ Temp.°C</th>
<th>$\Delta E_a$</th>
<th>$\beta_2$ Temp°C</th>
<th>$\Delta E_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4%</td>
<td>44</td>
<td>61</td>
<td>-71</td>
<td>14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1%</td>
<td>61</td>
<td>79</td>
<td>-60</td>
<td>16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.07%</td>
<td>59</td>
<td>92</td>
<td>-58</td>
<td>17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>original</td>
<td>59</td>
<td>97</td>
<td></td>
<td></td>
<td>-86</td>
<td>10</td>
</tr>
<tr>
<td>reprecipitated</td>
<td>61</td>
<td>104</td>
<td></td>
<td></td>
<td>-72</td>
<td>11</td>
</tr>
<tr>
<td>annealed</td>
<td>65</td>
<td>101</td>
<td></td>
<td></td>
<td>-86</td>
<td>11</td>
</tr>
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Figure 6.1 RIM mechanism of Nylon-6 polymerization
Figure 6.3 Mechanical spectrum of RIM Nylon-6 (freq. 10 rad/s)
Figure 6.4 Mechanical spectra of Nylon-6 with 0.4%, 0.1% moisture content (freq. 10 rad/s)
Figure 6.5 Dynamic loss spectra of Nylon-6 with different level of moisture content (freq.10 rad/s)
Figure 6.6 Log $\omega$ - $1/T$ plot of the $\beta$ processes
Figure 6.7 Frequency sweep of Nylon-6 sample with 0.07% moisture
Figure 6.9 Log $\omega - 1/T$ plot of $\beta_1$ process

- $E_a=14.4$ kcal/mole
- 16.5
- $T_0=1.01$ kK
- $T_0=0.7$ kK
- $T_0=0.4$ kK
Figure 6.10 Moisture effect on $\beta_1$ process
Figure 6.11 Log $\omega - 1/T$ plot of a process
Figure 6.12 Moisture effect on α process
Figure 6.13 Annealing effect on the Nylon-6 mechanical spectrum
Figure 6.14 Subtraction spectrum of X-ray differactions
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