Characterization and structure-property relationships in aliphatic polycarbonates

Sudhir Dattatraya Thorat

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To the Graduate Council:

I am submitting herewith a thesis written by Sudhir Dattatraya Thorat entitled "Characterization and structure-property relationships in aliphatic polycarbonates." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.

Paul J. Phillips, Major Professor

We have read this thesis and recommend its acceptance:

R. S. Benson, K. M. Kit

Accepted for the Council:
Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)
To the Graduate Council

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Accepted for the Council

[Signature]

Associate Vice Chancellor and Dean of The Graduate School
CHARACTERIZATION AND STRUCTURE-PROPERTY
RELATIONSHIPS IN ALIPHATIC POLYCARBONATES

A Thesis
Presented for the
Masters of Science Degree
The University of Tennessee, Knoxville

Sudhir Dattatraya Thorat
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ABSTRACT

Aliphatic polycarbonates are a family of thermoplastics with a wide variety of properties and applications. The knowledge of structure-property relationships of these homologues is important to design the formulation that will produce the desired properties at the given operating conditions. The objective of the work is to characterize these polymers and correlate their properties with their structure. Specifically, relationships between the thermal, mechanical, rheological and viscoelastic properties to the molecular structure of the polymers is discussed.

Using the Differential Scanning Calorimeter (DSC) we found that the polymers are completely amorphous. We characterized the glass transition temperature and the thermal degradation properties of the polymers using the DSC. It was found that the glass transition temperature decreases with the decrease in the chain stiffness or increase in the length of the side groups present. The thermal degradation was also studied using the Thermo-Gravimetric Analysis. It was found that the polymers degrade completely with less than 10% residue. The degradation temperature increases with the increase in the hydrocarbon content of the polymer chain.

The tensile testing of the bulk samples showed that the mechanical properties are a strong function of the structure of the polymer. The polymers behave from highly rigid and brittle to rubbery at the room temperature depending on their structure.
effect of strain rate on the mechanical properties is also studied for one polymer. Dynamic Mechanical Analysis was used to study the relaxation phenomena in the polymers. The glass transition temperatures were found to be greater than those obtained from Differential Scanning Calorimetry. The activation energies and the entropies of the primary relaxation are correlated to the structure of the polymers.

The Melt Flow Index studies were done on two polymers and the effect of the temperature was studied. The effect of the processing temperature on the surface roughness was studied for one polymer. The rheological properties were determined using parallel plate Rheometer. The effect of branching of the polymer and the molecular weight distribution on the rheological properties of the polymers is studied. These studies are important for the process design and product development using aliphatic polycarbonates.
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Chapter 1

INTRODUCTION

The reason for the very high toughness of the bisphenol-A-polycarbonate is the secondary relaxation process, which occurs as much as 200 °C below the glass transition temperature [1]. The molecular motions that are responsible for the relaxation processes are associated with the carbonate group present in the backbone of the polymer. Recognizing this attribute of the carbonate group makes the production of the polymers with that group potentially attractive. The structure and the properties of the resulting polymers will depend on the carbonate content of the resulting polymer, which acts as a flexibilizing unit.

Considerable interest has been displayed in recent years in utilization of CO₂ as the raw material for the production of polymers and other compounds. This interest stems from the necessity to fight the greenhouse effect and the fast exhausting carbon raw material resources [2]. In this study the characterization of the aliphatic polycarbonates manufactured from atmospheric CO₂ has been carried out using various characterization techniques and the relationship between the structure and the properties of the polymers is elucidated.
Aliphatic polycarbonates have found uses in various applications. They are being used as cost-effective additives for improving the printability and processing properties of polyolefins in thermoforming [3]. It is reported that by mixing 3% wt polypropylene carbonate to polypropylene the shrinkage of the calendered polymer reduced by 5.5% and the moldings showed significantly improved stability and printability. Recently [4] they have been used as additives for the polymers to improve their barrier properties with regard to gases, water vapor and aromas. Aliphatic polycarbonates are incorporated in the amounts of 2.5-7% wt with polypropylene, LDPE, PET and aromatic PC. They are also used as binders in metals/ceramic areas. The key properties contributing to this application are low decomposition temperatures, very low ash residues and clean products of combustion. The low dielectric constant, strong abrasion resistance, clarity and improved barrier properties have paved the way for these polymers in the coatings and packaging industry.

1.1. Objectives:

The main objective of this study is to analyze the behavior of aliphatic polycarbonates under different experimental conditions and to understand the relationship between their structure and the properties under those conditions. Polymer samples of designed chemical structure synthesized using particular monomers are obtained. This designed structure will give rise to tailored properties.
in the bulk samples. Typically we have investigated the thermal, viscoelastic, mechanical and rheological properties of these polymers

Aliphatic polycarbonates have been around for a considerable time [5] These polymers have developed commercial applications recently The knowledge of the structure-property relationships over a wide range of polymers of this category will be valuable for the design of product and processes and finding new applications using these polymers
Chapter 2

THEORETICAL BACKGROUND AND LITERATURE REVIEW

Industrially speaking polymers are divided into three types: plastics, fibers, and rubbers [6]. This includes both synthetic as well as natural products such as cellulose plastics, protein fibers, and natural rubber. The plastics are further classified as thermoplastics and thermosets. Thermosets are cross-linked polymers, which will not melt and flow. Thermoplastics are not cross-linked (they may be branched or linear) and in most instances will melt and flow when heated. Based on economic considerations, the thermoplastics are classified as commodity i.e., high volume-low price plastics, engineering i.e., low volume-medium price plastics, and specialty i.e., low volume-high price plastics.

Fibers are classified into synthetic and natural fibers. The synthetic fibers consist of cellulosic and non-cellulosic fibers. Rubbers or elastomers are classified into synthetic or natural rubber. Most of them have a network structure. The non-network elastomers formed by physical cross-linking are also commercialized and are called as thermoplastic elastomers.

One can use the same polymer in the form of a plastic and also as a fiber or elastomer by changing its structure and processing history. Fibers must exhibit the greatest strength of all these polymer types. The adhesives and coatings industries
use complex mixtures of polymers, solvents and additives depending on the application. The system of aliphatic polycarbonates comes under the category of engineering thermoplastics. Depending on their glass transition temperature they will behave as a glassy or elastomeric material. Some of these polymers may act as specialty polymers with higher costs depending upon the raw materials and the volume of production.

2.1. **Structure of polymeric solids:**

Polymer molecules are large molecules consisting of repeating units joined together by covalent bonds. The polymers of different types of monomers are called copolymers. The polymeric solids exhibit different types of structures at different levels.

2.1.1. **Chemical Structure:**

The specific arrangement of atomic groups within the chain of the polymer molecule constitutes its chemical or atomic structure. Many factors decide the chemical structure of the polymers, the most important being the type of raw materials (monomers) used and the mechanism and catalysts used for polymerization. The polymers are classified depending on the mechanisms of polymerization reactions as shown in figure 21.
Figure 2.1. Classification of Polymerization Reactions.
Different polymerization processes give rise to differences in molecular weight and its distribution, end groups, stereochemistry and chain branching, which will affect the mechanical and physical properties of the polymers. This can be exemplified by considering polyethylene. HDPE prepared at low pressures using co-ordination catalysts is linear, denser, stronger and higher melting polymer than LDPE which is prepared at high pressures using free radical polymerization.

Isomerism is one of the most important features in the chemical structure of the polymers. Isomerism is the phenomenon when two or more molecules have the same molecular formula and different structural formulae. Different isomers encountered in the polymers are positional isomers, steric isomers, structural & geometric isomers, and rotational isomers as explained by McCrum et al. [7].

Chemical structure of the polymers also incorporates the larger scale effects such as chain branching and cross-linking. Another technique to manipulate the chemical structure of the polymer chain is to polymerize two or more comonomers to form a copolymer. In the case of two comonomers we can have alternating, random, block or graft copolymers. Although the structure of the polymers is normally represented as the repeat unit repeated many times, they may also incorporate unsaturated structures, chain branches, reactive chain ends and variety of other features formed due to the polymerization process or due to the impurities present in the reactants. Moreover the polymer can also undergo structural changes during its shelf life due to
the effect of sunlight and air. These abnormal structures may act as the centers for the initiation of the degradation process and thereby making polymers less stable than anticipated [8].

2.1.2. Physical structure:

Segments of the polymer chain can exist in either crystalline or amorphous form. Polymer chain can only crystallize if it has a regular chemical structure e.g., in homopolymers and alternating copolymers. However, the bulk polymer can never be 100% crystalline. It can either be semi-crystalline or amorphous. There are three views regarding the physical structure of amorphous polymers. Flory [9] views that there is no physical structure in the amorphous phase and the chains have unperturbed dimensions of the random coil. Kargin [10] supported the idea of ordered structure in the amorphous phase. A compromise position allowing some local order but overall random coil dimensions is represented by Privolko [11]. Lindenmeyer [12] proposed that there exists a short range order with moderate irregular chain folding in the amorphous state and the molecule interacts with 5-10 other macromolecules instead of 50-100 as in the random coil situation.

Semi-crystalline polymers can be crystallized under the influence of stress or from the melt or solution. The concept of folded chain crystals was proved from the discovery of solution grown single crystals of polyethylene [13]. The sketch of the
basic microstructure in the crystallites is as shown in the figure 2 2 [14]. The crystallinity and the rate of crystallization of polymers depend on the chemical structure i.e. tacticity, branching, comonomer content, molecular weight and its distribution [15] and processing conditions such as temperature (for isothermal crystallization), pressure, solvent and other additives lie nucleating agents etc. [16]

2.1.3. Significance of structure of polymers:

The morphology and the chemical constitution of the polymers decide most of the desirable properties of the polymers. Many of the unique properties of the polymers are due to the flexibility of the long chain molecules conferred by the internal rotation around C-C bonds. This rotation provides mechanism for the flow of polymer in the liquid state, the transport of mass and rotation of dipoles in the solid state. The properties of the polymers are dependent on the structural order exhibited by the molecules. The dissymmetry arising from the existence of isomers, branching or cross-linking will reduce the degree of crystallinity by hindering the parallel packing of the chain segments.

Variations in the stereoregularity have a large effect on the properties e.g. polystyrene is an amorphous solid when prepared from the free-radical methods while stereoregular isotactic polystyrene is prepared using Ziegler-Natta catalysts is semi crystalline. The geometric configuration of the structural units also influences
Figure 2.2 Sketch of the basic crystallite microstructure of the semi-crystalline polymers [16].
the properties of the polymers e.g. cis-1, 4-polyisoprene is an amorphous rubber while trans-1,4-polyisoprene is semicrystalline [7]. The structure of the polymer also decides the thermal properties such as the glass transition temperature [17], melting temperature [15], thermal stability, mechanical and rheological properties of the polymers. Hence study of structure-property relationships is of utmost importance for product development and safe & efficient process design for the given product.

2.2. Transitions in Polymeric Materials:

Polymers exhibit unique properties due to their macromolecular structure and the flexibility of these macromolecules. Occurrence of various transitions in the macromolecules is one of these unique properties. When we heat the polymer from a very low temperature, it undergoes solid-state secondary transitions due to localized bond movements in the chains. These movements have been studied and classified as β, γ and δ transitions [18].

As heating continues we reach the glass transition temperature or Tg where the chains in the amorphous region begin to co-ordinate large-scale motions. Since Tg occurs only in the amorphous phase we do not see glass transition in 100 % crystalline materials. Continued heating brings us to the Tα* that occurs in the semi-crystalline polymers due to the slippage of crystallites. In some amorphous polymers we get TII due to the motion of the coordinated segments in the amorphous phase leading to...
reduced viscosity. Haward [19] gives different types of transitions that might occur in the amorphous phase of the polymers above Tg. Finally we reach melting temperature Tm where large chain slippage occurs and the material flows. In the case of cured thermosets, no melting occurs and the material degrades after heating to temperatures above Tg. An idealized temperature scan of a polymer is shown in figure 23. [20]

2.2.1. Theories of Glass Transition:

The glass transition has a rate-dependent aspect as well as an underlying fundamental thermodynamic basis. Theories of the glass transition invariably treat the observed value of glass transition as the kinetic (rate-dependent) manifestation of the underlying thermodynamic phenomenon. However, there has been considerable controversy for the theoretical and fundamental explanation of the glass transition. The thermodynamic theories consider the glass transition to be an underlying but true second order transition while kinetic theories rely on the relaxation processes existing in the materials which, due to the difficulty in making measurements at very long times, give rise to the glass transition artifact [19]. Bicerano [21] gives the definition of glass transition temperature (Tg) at practical and operational level as "the temperature at which the forces holding the distinct components of an amorphous solids together are overcome, so that these components become able to
For purely crystalline materials, no \( T_N \) occurs. 

Beta transitions are often related to the toughness.

Rubbery plateau is related to \( M_g \) between crosslinks or entanglements.

For thermosets, no \( T_m \) occurs.

Figure 2.3. Idealized temperature scan of a polymer [21].
undergo large scale viscous flow, limited mainly by the inherent resistance of each component to such flow. “

2.2.1.1. Relaxation Theories:

The relaxation of a polymer primarily involves conformational changes by rotation about the single bonds in the main-chain. Bond rotation is hindered by the potential energy barriers and therefore is a thermally activated process dependent on the chain stiffness. The rate of change from one rotational isomeric conformation to another is given by the usual Arrhenius activation energy concept. In the case of relaxation in the bulk amorphous phase, where the molecules are packed closely together, the above process requires also the co-operative motion of the motion of the segments of several neighboring chains [22]. The causes of these local structural changes are the intermolecular van der Waal forces that are related to the cohesive energy density.

When the temperature is lowered the cooperative motion slows down quickly, until a temperature is attained where relaxation cannot be detected within the time scales usually used (minutes to days). This temperature is \( T_g \) measured by “static” scanning techniques like dilatometry. As you increase the scanning rate the \( T_g \) increases and it is quite evident that the glass transition is a kinetic phenomenon. Whatever may be the molecular origin of the relaxation, the effect is observed when the relaxation time of the molecular motion responsible for the transition matches the observational frequency at the temperature of the experiment. The energy barrier theories of simple
Arrhenius type are insignificant by themselves to explain the experimental facts. In addition to the thermal energy available and the energy barrier restricting the rotation, there are considerations of packing and interactive forces with other molecules to take into account [19]

2.2.1.2. Thermodynamic Theories:

Kauzmann [23] showed that the point of intersection of the entropy-temperature curves for the supercooled liquid and the crystalline state that will lie between 0 K and $T_g$ is regarded as a thermodynamic glass transition temperature. Gibbs and DiMarzio [24] have advanced a novel approach for the polymeric materials for which it is usually not practicable to measure and compare the specific heats of the crystalline and supercooled liquid states. They assumed that there would be a second order transition at the temperature $T_2$ at which the configurational entropy of the system becomes zero. The rapid increase in the relaxation times on cooling near $T_g$ is contributed to the lack of configuration available. This theory was successful in describing the relationship of molecular weight, copolymerization, plasticization and cross-linking on transitions. Adam and Gibbs [25] developed a molecular-kinetic theory dealing with the temperature variation of the size of the cooperatively rearranging region in the glass-forming liquids, which was shown to be a function of configurational entropy. Adam and Gibbs theory provides an alternative approach to account for the observed behavior of the polymers near the $T_g$ that do not rely on the free volume assumptions which will be discussed later.
2.2.1.3. Free Volume Theories:

Fox and Flory [26] advocated a semi empirical but outstandingly successful approach for the molecular interpretation of the glass transition. Any material has its volume partly occupied by the molecules and the remaining volume is free or unoccupied. It is supposed to consist of holes of molecular sizes or imperfections in the packing order of molecules that arises from their random array. In order to adjust from one conformational state to other, the molecules must be able to move into this unoccupied volume. The glass transition temperature for any polymer is the one at which the free volume reaches a critical value below which there is insufficient room for molecular motion by rotation or translation.

The distribution of the free volume within the glass will remain fixed below Tg. The glass will however expand with the increasing temperature due to normal expansion process of the molecules due to changing vibrational amplitudes of the bond distances. Above the glass transition the free volume will itself expand which will result in larger expansion of rubber than glass. The situation is represented in figure 24 [19]. The shaded area in the figure represents the available free volume (V_f) in the glassy state.

If V_o is the occupied volume of the glass at the absolute zero and V_g is the total volume at the glass transition temperature Tg, then
Figure 2.4 A schematic illustration of the free volume and expansivities \((dV/dT)_g\), \((dV/dT)_r\), in the glassy and rubber states respectively [20].
\[ V_g = V_f + V_o + \left( \frac{dV}{dT} \right)_g T_g \]  

(21)

Where, \( V_f \) is the frozen in excess volume because of the molecular immobility in the glassy state. Similarly at the temperature above the glass transition (\( T > T_g \)) the volume of the rubbery phase \( V_r \) is given by

\[ V_r = V_g + \left( \frac{dV}{dT} \right)_r (T - T_g) \]  

(22)

The expansion of the free volume alone =

\[ \left( \frac{dV}{dT} \right)_f - \left( \frac{dV}{dT} \right)_g \]  

(23)

The Williams-Landel-Ferry (WLF) theory [27] uses a perhaps more widely used definition of the free volume. This theory has been successful in relating relaxation times at a temperature \( T \) to the standard reference temperature (usually \( T_g \)), at least over the range from \( T_g \) to \( T_g + 100 \). This form usually represents it

\[ \log a_T = \frac{-C_1(T - T_g)}{C_2 + T - T_g} \]  

(24)

Where,

\[ a_T = \frac{\tau(T)}{\tau(T_g)} \]  

is the ratio of relaxation time at the given temperature \( T \) to that at \( T_g \).

The function \( a_T(T) \) is important to describe the physical properties of the polymer system because it reflects the temperature dependence of the segmental friction coefficient or mobility on which the rates of all configuration rearrangements
depend. The empirical constants $C_1$ and $C_2$ may vary with the specific polymer, but are usually close to the universal values $C_1=17.44$ and $C_2=51.6$ K.

It can be seen that the above equation predicts infinite log $a_T$ at some temperature $T_\infty$ given by

$$T_\infty = T_g - C_2$$ (25)

Williams [28] suggested the following relationship for the empirical constants dependence of viscosity arising largely from its dependence on free volume

$$C_1 = \frac{1}{(2.303 f_g)}$$ (26)

$$C_2 = \frac{f_g}{\alpha_f}$$ (27)

Here, $f_g$ is fractional free volume at $T_g$, and $\alpha_f$ is the relative free volume expansion coefficient. Comparing the above equations with the “universal” variables $C_1$ and $C_2$ yield $f_g = 0.025$ and $\alpha_f = 4.8 \times 10^{-4}$ K$^{-1}$. The fractional free volume is known to be the fraction of the bulk volume not actually occupied by the polymer chains, but $f_g$ is not well defined. The coefficient $\alpha_f$ is approximated by $\Delta \alpha$, the difference between the thermal expansion coefficients above and below the $T_g$.

The theories of Adam and Gibbs [25] avoid the difficulties surrounding the free volume figure of 0.025.

### 2.2.2. Secondary transitions:

Similar nomenclature is used for the transitions in the semicrystalline and amorphous polymers. According to Duetsch et al [29] the glass transition is designated by the
Greek alphabet $\alpha$ with $\beta$, $\gamma$, $\delta$, $\varepsilon$ representing secondary sub-$T_g$ transitions in decreasing order of temperature. To assign the molecular motion responsible for each transition we need to investigate each polymer system individually.

For secondary transitions, the motion over the restricted lengths of few carbon atoms (six to eight) must be occurring in some way and the following theories have been proposed to explain the secondary transitions.

### 2.2.2.1. Local Relaxation Mode Theory:

Due to the rotational energy barrier, the small scale motions of short chain segments can occur only by a limited vibrational oscillation about their mean position, which will show up as secondary relaxation [30]. Due to large number of internal degrees of freedom of the polymer backbone, the frequency spectrum of normal vibrations will be broad. The low frequency, high amplitude modes of vibration will be dampened due to the high internal friction in the glassy state. The low amplitude, high frequency modes will retain their vibrational character. These motions are different from the translational modes or the micro Brownian motion responsible for the glass transition. The local relaxation mode theory explains the breadth of the $\beta$ relaxation region, normal Arrhenius dependence of the activation energy and insensitivity of the relaxation on the pressure.
2.2.2.2. The Crankshaft Theory:

Schatzki [31] suggested that in the amorphous polymers containing methylene linkages, the seventh and the first bonds were collinear and the intervening atoms could rotate along the chain axis without disturbing any chain atoms further along the chain. The activation energy for this 'crankshaft' rotation is in agreement with the observed values. It includes the intrachain energy barrier as well as the surrounding matrix energy barrier due to van der Waals' interaction. Boyer [32] and Wunderlich [33] have also proposed models of various crankshafts. The serious drawback of the crankshaft models is that the free volume needs to be created in order the crankshaft may rotate. However, the secondary transitions, unlike $T_g$, are insensitive to reduction in free volume.

2.2.2.3. Association-dissociation theory:

Andrews [34] proposed that the solid-state transitions represent merely the loosening of various types of secondary intermolecular cohesive bonding in the solid state. The association-dissociation processes that are involved are governed by ordinary thermodynamic equilibrium and the frequency dependence associated with the transition is related to the transport rate in the two directions of such equilibrium. This theory can also be extended to cover the glass transition as well.
In addition to the main chain movements over the shorter lengths, the secondary relaxation can also arise from the side group motion referred to as the $\gamma$ relaxation. The amplitude and the frequency of these side chain motions depend on the nature and the size of the side group and its interactions with its neighboring units in the main chain. If the side group is the flexible one such as a long pendent alkyl groups chain, then a local mode type of motion is possible irrespective of the mobility of the main chain. The cyclohexene ring undergoes transition between its isomeric conformations giving rise to relaxation region. The aromatic rings are also associated with a limited motion of various kinds, which can induce a small relaxation peak.

2.2.3. Significance of Polymeric Transitions:

The glass transition affects the thermodynamic, physical, chemical, electrical and mechanical properties of the polymers to such an extent that it defines one end of the temperature range over which the polymer can be used or processed. From the WLF equation, it can be proved that closer the polymer to its $T_g$, the larger the temperature sensitivity of its melt viscosity [35]. Hence polymers like polystyrene, polyvinyl chloride, polycarbonates exhibit high temperature sensitivity in processing, while polyethylene, polyamides, polypropylene are processed at more than 150°C above their glass transition temperature and show small temperature sensitivity.
The sub-$T_g$ transitions affect the material properties in the glassy state. The $\beta$ relaxation, which reflects the localized motion in the chain that absorbs enough energy, is often correlated with the impact resistance or the toughness of the polymer. However, this is not always the case as in the case of rubber-latex-modified polystyrene, higher impact strength is by virtue of change in the craze and crack propagation mechanism rather than direct energy absorption [36]

The secondary relaxation regions do influence the creep and stress relaxation properties of the glassy polymers and hence the long term stability of the rigid construction polymers. The yield stress behavior of the glassy thermoplastic also shows some dependence on the presence of secondary dispersion regions. The $\beta$ relaxation can also be considered as the activation barrier for solid-phase reactions, deformation flow or creep, acoustic damping, physical aging changes and gas diffusion into polymers as the activation energies for these processes and the $\beta$ transition are similar [37]

2.3. Viscoelasticity and Rheology:

The elastic solid stores all the energy during the deformation and reverts instantaneously to its original dimensions when the deformation forces are removed. The viscous liquid flows irreversibly under the action of external forces and does not store any energy. Polymers are viscoelastic i.e., they display all the intermediate
properties between the elastic solid and the viscous liquid depending upon the operating conditions. The mechanical and the rheological properties of the polymers are sensitive to the type, rate, duration and frequency of loading, temperature and relative humidity. Table 2.1 lists typical loading and operating conditions with the corresponding material properties a designer needs to consider [38].

2.3.1. Linear Viscoelastic Behavior:

The common phenomena occurring due to the time dependent behavior of the polymeric materials is creep and stress relaxation. When the polymer is loaded in shear or extension, it will show an instantaneous deformation as expected for a Hookean solid, followed by time dependent continuous deformation called "creep". In the stress-relaxation, when the polymer is subjected to step change in strain, the stress relaxes with time. In the case of viscous liquid the stress relaxes to zero instantaneously whereas in the elastic solids the stress will remain constant. The ratio of instantaneous stress to constant strain is called relaxation modulus

\[ G(t) = \frac{\tau(t, \gamma)}{\gamma} \]

If G(t) is plotted against t, all the data will fall on the same curve for small strains, typically \( \gamma < \gamma_c < 0.5 \) for polymeric liquids. The relaxation modulus is independent on strain (in other words the relaxation stress is linear function of strain applied) and hence the phenomenon is called linear viscoelasticity.
Table 2.1. Typical loading/operating conditions together with the relevant material properties.

<table>
<thead>
<tr>
<th>Operating/Loading Conditions</th>
<th>Material Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short-term loading</td>
<td>Stress-strain behavior (only elastic response)</td>
</tr>
<tr>
<td>Long-term loading</td>
<td>Creep and stress relaxation (Viscoelastic-time dependent response)</td>
</tr>
<tr>
<td>Repeated Loading</td>
<td>Fatigue</td>
</tr>
<tr>
<td>High velocity and impact loading</td>
<td>Impact strength</td>
</tr>
<tr>
<td>Loading at extreme temperatures</td>
<td>Thermal mechanical behavior</td>
</tr>
</tbody>
</table>
For higher strains, the stress is not a linear function of strain and the relaxation modulus is given by:

$$G(t, \gamma) = \frac{\tau(t, \gamma)}{\gamma}$$ \hfill (2.9)

This behavior is termed as non-linear Viscoelasticity.

Different models have been put forth to explain the linear viscoelastic behavior of the polymers and have been explained in books by Ward et al [39] and Bird et al [40].

### 2.3.2. Small Strain Material Functions:

Different small strain used in the linear viscoelastic region are stress relaxation, creep and sinusoidal oscillations. The creep data is useful for the long time end of the relaxation spectra. In a creep experiment the stress is increased instantly from 0 to $\tau_0$ and the strain is recorded versus time. In the linear viscoelastic region the strain is linearly related to stress and the creep compliance is defined as

$$J(t) = \frac{\gamma(t)}{\tau_0}$$ \hfill (2.10)

$J(t)$ has the units of reciprocal modulus but in general it is not equal to $1/G$.

Another type of experiment done in the conjunction with the creep is the creep recovery, the recoil of strain when the stress has been removed.
In the sinusoidal oscillations the sample is deformed sinusoidally and often within few cycles of start up the stress will also oscillate sinusoidally at the same frequency but in general shifted by a phase angle $\delta$ with respect to the strain wave [41].

This can be expressed mathematically as

$$\gamma = \gamma_0 \sin \omega t$$  \hspace{1cm} (2.11.)

$$\tau = \tau_0 \sin (\omega t + \delta)$$  \hspace{1cm} (2.12.)

The stress wave is decomposed into two waves of the same frequency, one in phase with the strain wave and one 90$^\circ$ out of phase with this wave. Thus,

$$\tau = \tau' + \tau'' = \tau_0' \sin \omega t + \tau_0'' \cos \omega t$$  \hspace{1cm} (2.13.)

$$\tan \delta = \frac{\tau_0''}{\tau_0'}$$  \hspace{1cm} (2.14.)

This decomposition suggests two dynamic moduli:

$$G' = \frac{\tau_0'}{\gamma_0}$$  \hspace{1cm} (2.15.)

Which is the in-phase or elastic modulus, and

$$G'' = \frac{\tau_0''}{\gamma_0}$$  \hspace{1cm} (2.16.)

Which is the out-of-phase, viscous or loss modulus.

We can also write,

$$\tan \delta = \frac{G''}{G}$$  \hspace{1cm} (2.17.)
The prime and double prime notations are originated from the complex numbers. We can represent \( \gamma = \text{Imaginary part of } \{ y_0 e^{i\omega t} \} \) and likewise \( \tau' = \text{Im } \{ \tau_0 e^{i\omega t} \} \) and \( \tau'' = \text{Re } \{ \tau_0 e^{i\omega t} \} \). Then we define \( G^* \) such that

\[
\tau_0 = |G^*| \gamma_0 \tag{218.}
\]

Where \( G^* \) is a complex number with \( G' \) as its real part and \( G'' \) as its imaginary part,

\[
G^* = G' + iG'' \tag{219}
\]

Hence,

\[
\tau = G'\gamma_0 \sin \omega t + G''\gamma_0 \cos \omega t \tag{220}
\]

Physically speaking, \( G' \) and \( G'' \) represent the energy stored and dissipated respectively per cycle of deformation per unit volume.

For dealing with the liquids, sinusoidal strain rate is used and the dynamic viscosity material function is defined \([40]\). Noting that the derivative of the small strain is the strain rate, we have

\[
\gamma = \frac{dy}{dt} = \gamma_0 \omega \cos \omega t = \gamma_0 \cos \omega t \tag{221}
\]

If we decompose the stress again, the \( \tau'' \) wave will be in phase with strain rate wave \( (\gamma) \) and out of phase with the strain wave \( (\gamma) \). From the magnitudes of the viscous stress to the strain rate, we can define the dynamic viscosity as:

\[
\eta^* = \frac{\tau''}{\gamma_0} = \frac{G''}{\omega} \tag{222}
\]

The elastic part of the complex viscosity is defined as:

28
The magnitude of the complex viscosity is given as

$$|\eta^*| = (\eta'^2 + \eta''^2)^{1/2} = \left[ \left( \frac{G''}{\omega} \right)^2 + \left( \frac{G'}{\omega} \right)^2 \right]^{1/2} = \frac{1}{\omega} |G^*|$$  \hspace{1cm} (2.24)

It is possible to define other small strain material functions such as stress growth at constant rate of shearing or recoverable strain after constant strain rate. However, these deformation histories are better suited for large strain studies.

**2.3.3. Shear thinning behavior:**

For most of the polymeric systems it has been observed that the apparent viscosity which is given by the formula

$$\eta = \frac{\tau}{\gamma}$$  \hspace{1cm} (2.25)

depends on the shear stress and the shear rate and hence the polymers are non-Newtonian fluids. The complete molecular-kinetic consideration of the structural considerations of the nature of non-Newtonian viscosity of polymers is associated with their network structure. In polymers, the enormous molecular length coupled with the flexibility of the chains and presence of inter- and intramolecular interactions leads to the formation of the various structural linkages like nodes, junctions (entanglements), as a result of which the system as a whole is a three...
dimensional network. In a state of rest the linkages are formed and destroyed by thermal motion, so that at constant temperature a dynamic equilibrium is established. When the polymer is deformed, there will be some disentanglement, slippage of chains over each other, and molecular alignment in the direction of the applied stress. As a result, the resistance exhibited by polymer to flow decreases with the deformation, due to the evolution of its microstructure (which tends to align in the flow direction). This is often referred to as shear thinning behavior.

2.3.3.1. Flow behavior and structure of polymer:

The non-Newtonian viscosity of the polymer is not only of practical interest but also a theoretically important phenomenon since it is intimately connected with the structural specificity of polymeric system [42]. The viscosity of the polymer in steady state is a function of operating conditions such as temperature and pressure but also the molecular mass, distribution of molecular mass and the branching of polymers. The zero shear viscosity (or the largest Newtonian viscosity or initial viscosity) $\eta_0$ increases with the increase in the molecular weight of the polymer. There exists a critical molecular weight ($M_c$) for a given polymer where spatial network of junctions (macromolecular entanglements) appear in the polymer and initial viscosity becomes a strong function of the molecular weight. The critical molecular weight is a function of temperature.

30
The molecular mass distribution (MMD) also affects the viscosity of samples with identical weight average molecular weight ($\bar{M}_w$). This is because the non-Newtonian behavior is a relaxation effect and depends therefore on the form of the relaxation spectrum, which is further determined by the MMD. With a considerable broadening of MMD, the spatial inhomogeneity of the entanglement network increases. With the broadening of MMD to the side of high molecular masses, the shear rates and the stresses at which non-Newtonian behavior are observed are decreased. When the shear rate increases, the critical shear rate is attained for the high molecular mass component, which is equivalent to its transition to rubbery state and it behaves like rubbery filler. This reduces the apparent viscosity and also the dissipation losses. In this case, the stored recoverable deformation of the high molecular mass component increases with the increase in the stress, which is typical of rubbery polymers. Because of this, in the polydisperse polymers containing high molecular mass components, all the effects due to large recoverable deformations are more strongly pronounced, say, the development of normal stresses and the die-swell.

The effect of branching on the viscosity of the macromolecules can be understood if one takes into account the manner in which the mean radius of gyration of the unperturbed macromolecular coil varies under the influence of the branching. This is expressed with the aid of the conformational parameter or g-factor.
The condition under which an entangled network is formed depends on the characteristics of the branching of the polymeric chain. It is observed that the decrease in the viscosity of the branched polymer as compared to the linear polymers of the same molecular mass occurs when the length of the side branches does not exceed certain critical value. The effect of the long chain branching on the rheological properties of polyethylene has been studied frequently [43] while some doubt exists on the influence of the short chain branching. Valenza et al. [44] have studied the effect of short chain branching on the rheological properties of a wide series of LLDPE samples polymerized in the presence of different co-monomers.

They found no large differences in the flow curves of the polymers of the same molecular weight due to the change in the comonomer. They found that the activation energies are independent of the shear stress and the zero shear viscosity over the whole series appears unaffected by the side chain length. They found the critical shear rate to be slightly dependent on the co-monomer type but strongly affected by the molecular weight. The presence of long chain branching causes an abnormal sharp increase in the viscosity which is associated with the fact that the principal factor here is not the change in the size of macromolecule but the enhanced intermolecular interactions caused by the entanglements and the side branches.
2.4. Aliphatic polycarbonates:

Aliphatic polycarbonates or Poly (alkylene carbonates) were first synthesized at Tokyo University in 1969 by Inoue et al. [5] by the ring opening polymerization of epoxides such as alkylene oxides, epichlorohydrin and styrene oxide with CO₂ using the organozinc catalyst

\[
\begin{align*}
\text{CH}_2 - \text{CH} & \quad + \quad \text{CO}_2 \\
\text{O} & \quad \text{catalyst} & \quad \text{O} & \quad \text{catalyst} \\
\end{align*}
\]

In the copolymerization of carbon dioxide and monosubstituted epoxides, the alternating copolymer formed may have various isomeric structures in terms of head-to-tail or head-to-head linkages. The CO₂–propylene oxide copolymer has proved to have a regular head-to-tail structure formed as a result of selective cleavage of methylene-oxygen bond. Other epoxides with alkyl or aralkyl substituents are also cleaved at the methylene-oxygen bond [45]. There are two types of nomenclature systems existing for aliphatic polycarbonates. The polycarbonate synthesized using certain alkylene oxide and CO₂ is either termed as poly (alkylene) carbonate or alkylene polycarbonate. Hence aliphatic polycarbonate manufactured from propylene oxide and CO₂ is called poly (propylene) carbonate or propylene polycarbonate.

The other routes for the manufacture of aliphatic polycarbonates are as follows

1) Direct condensation of diols or alkali metal diolates with CO₂ using crown ethers [46] or tin [47] catalysts
2) Carbonate interchange reaction of aliphatic diols and dialkyl carbonates [48, 49]

3) The reaction between aliphatic diols and phosgene [48]

4) The ring opening polymerization of cyclic carbonates [50] using nucleophilic initiation [51].

5) Lipase catalyzed ring-opening polymerization of 5-Methyl-5-benzyloxycarbonyl-1, 3-dioxan-2-one [52]

Various catalytic systems such as diethyl zinc-water [53], rare earth metal coordination catalysts 54, 55], zinc carboxylate [56], metal amides [57], Zinc hydroxide and carboxylic acids [58] and catalysts based on alkali metal compounds and pyrogallol [59] are reported for the copolymerization of alkylene oxides and CO2 to give polyalkylene carbonates. As mentioned earlier the change in the catalytic system not only changes the reaction conditions but also changes the structure and constitution of the product polymer and hence its properties. Ree et. al [60, 61] report the clean, green copolymerization of excessively loaded propylene oxide as a solvent with carbon dioxide using zinc glutarate catalyst. The polymer is obtained in the higher yield and the solvent and CO2 are fully recoverable and reusable.

It is reported [56] that certain rare earth metal catalyst system produces alternating copolymer while the other produces a random polymer. Recently reported are the zinc-based compounds with sterically bulky ligands that readily converted CO2 and epoxides to aliphatic polycarbonates under mild reaction conditions [62]. The
alternating copolymers with biodegradable properties were formed using these catalysts. Chen et al. [55] reported that certain rare earth metal catalyst systems produced copolymers with high molecular weight, narrow molecular weight distribution and a high thermal stability.

2.5. Characterization of aliphatic polycarbonates

2.5.1. Molecular Weights

Higher molecular weights and narrower molecular weight distribution is obtained with rare earth metal catalyst systems as compared to organometallic catalyst [54, 55]. Viscosity measurements [64], GPC measurements [48, 51, 56] and Vapor phase osmometry [48, 56] are used to determine the molecular weights of aliphatic polycarbonates synthesized using different routes. Pokharkar et al [48] mention that the polydispersity index of the polymers ranges from 2 to 3.

Intrinsic viscosity measurements using Ubbelohde viscometer are carried out with polymer solutions in CHCl₃ [45, 48, 64], benzene [55] and dimethyl sulfoxide [46]. Shu et al [64] report the following correlation of viscosity average molecular weight with intrinsic viscosity:

\[
[\eta](dl/g) = 6.64 \times 10^{-5} M_v^{0.76} \quad (26 \text{ C in CHCl}_3)
\]

The number average molecular weight is related as [55]:

\[
[\eta](dl/g) = 1.11 \times 10^{-4} M_n^{0.8} \quad (35 \text{ C in benzene})
\]
2.5.2. Thermal analysis and crystallinity

The DTA/TGA analysis of propylene oxide (PO) / CO₂ and ethylene oxide (EO) / CO₂ copolymers is reported in the literature [45, 53] The CO₂ / epoxides alternating copolymers decompose by moderate heating in the vicinity of 200 °C with rapid decrease in weight and heat absorption Thermally stable random copolymers with decomposition temperature are reported by Chen et al [55].

Houlihan et. al. [63] have synthesized tertiary polycarbonates which are unique in their thermolytic behavior, showing complete stability below a critical temperature and exhibiting a near-instantaneous and quantitative decomposition into volatile low molecular weight compounds above that temperature Nevertheless Inoue [45] mentions that the PO / CO₂ and EO / CO₂ copolymers can be molded at 140/ 150 °C without appreciable decomposition He also reports that these polymers are amorphous and have no clear melting points below the decomposition temperatures.

However, Pokharkar et al [48] reported semi-crystalline aliphatic polycarbonates prepared from aliphatic C₄, C₆, C₈ terminal diols and attributed the crystallinity to the ability of the longer carbon chains to undergo crystallization They also report the initial decomposition temperature (IDT), glass transition temperatures and melting temperatures of these polymers.
2.5.3. Degradability

Suyama et al. [65] report that aliphatic polycarbonates are stable against hydrolysis by water and were hardly hydrolyzed during the heat treatment with water at 120°C for 24 hours whereas aliphatic polyesters are easily hydrolyzed. Inoue [45] has studied the degradation of EO/CO₂ copolymer in air at 175°C (i.e., below its degradation temperature) using TGA and reported that the degradation is suppressed to some extent by adding a phenol derivative to the sample. He also reported that random hydrolytic scission of the EO/CO₂ occurs after heating in neutral water for several hours while the copolymer is hydrolyzed readily under alkaline conditions.

The biodegradation of aliphatic polycarbonates has been studied in reference to the medical applications. Suyama et al. [65] have studied the enzymatic degradation of polytetramethylene carbonate using esterase and lipase. They reported the GPC chromatograms of the incubated polymer with the enzymes in which the intensity of the peak in the large molecular region decreased along with the appearance of oligomeric peaks in the smaller molecular region. Zhou et al. [66] have reported the enzyme-catalyzed degradation of aliphatic polycarbonates with a single enzyme, *Rhizopus delemar* Lipase at 37°C in an acetate buffer solution.

Shu et al. [64] have studied the biodegradation of aliphatic polycarbonates by soil burial method. They reported that the presence of hydrolysable carbonate linkages in the polyethylene carbonate chains favors the biodegradation of the polymer.
case of terpolymer of EO/ PO/ CO₂ the biodegradability is influenced by the addition of the non-biodegradable PO units. The unsaturated polycarbonate of maleic anhydride/ EO/ CO₂ also showed degradation.
3.1. Materials

Dr. Viktor Semenov of Zelinsky Institute of Organic Chemistry, Moscow, kindly provided aliphatic polycarbonates used for this study. The polymers in this study were synthesized using the patented method of PAC POLYMERS INC. The method used zinc adipionate as catalyst under standard conditions of 25-35 atmospheres pressure and a temperature of 45-55°C. The polymers were synthesized using corresponding alkyl epoxides and CO₂ in standard conditions. The names and the chemical reactions used for the synthesis of the obtained aliphatic polycarbonates are as shown below:

\[
\text{n CH}_2\text{CH + n CO}_2 \rightarrow \text{CH}_2\text{CH-O-C-O}_n 3.1
\]

poly(ethylene carbonate)

\[
\text{n CH}_2\text{CH + n CO}_2 \rightarrow \text{CH}_2\text{CH-CH-CH}_2\text{CH-CH}_3\text{O}_n 3.2
\]

poly(propylene carbonate)

\[
\text{n CH}_2\text{CH + n CO}_2 \rightarrow \text{CH}_2\text{CH-O-C-O}_n 3.3
\]

linear pentene polycarbonate
The terpolymer prepared using 80 wt % cyclohexene oxide, 20 wt % propylene oxide and CO₂ was also obtained.

### 3.2. Molding and sample preparation

The Wabash hot press was used for compression molding the bulk samples into thin sheets. The temperatures used in the hot press for various samples are tabulated in table 3.1. The polymer was pressed in the kapton® films for about 1 minute and
Table 3.1. Temperatures used in the hot-press for the aliphatic polycarbonates

<table>
<thead>
<tr>
<th>Aliphatic polycarbonate</th>
<th>Hot-press temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly (ethylene carbonate)</td>
<td>190 °C</td>
</tr>
<tr>
<td>Poly (propylene carbonate)</td>
<td>200 °C</td>
</tr>
<tr>
<td>Linear pentene polycarbonate</td>
<td>150 °C</td>
</tr>
<tr>
<td>Linear hexene polycarbonate</td>
<td>150 °C</td>
</tr>
<tr>
<td>Linear octene polycarbonate</td>
<td>150 °C</td>
</tr>
<tr>
<td>Cyclo hexene polycarbonate</td>
<td>220 °C</td>
</tr>
<tr>
<td>Terpolymer</td>
<td>220 °C</td>
</tr>
</tbody>
</table>
quenched in the ice-cold water. The samples were obtained by cutting these thin sheets using razors for various experimental techniques used for their analysis.

3.3. Characterization:

3.3.1. Differential Scanning Calorimetry (DSC)

Thermal analysis of the samples was carried out in a Perkin-Elmer DSC 7 in a purging nitrogen atmosphere. After the baseline run without any samples in the pans, the instrument was calibrated for the melting onset and heat of fusion of pure indium. The 6 to 9 mg of sample is heated from −40°C to 340°C at the rate of 10°C/minute to observe the thermal behavior of the samples. The glass transition temperature is taken to be the temperature at the center of the transition. The degradation temperature is taken as the temperature of the peak of the curve. The isothermal studies were performed by heating the sample to a certain temperature and holding it at that temperature for a certain time.

3.3.2. Thermo-gravimetric Analysis (TGA)

Mettler thermo-gravimeter (TG50) was used to measure the mass of the samples subjected to a temperature program in a preselected atmosphere. The thermo-gravimeter was calibrated using automatic multiple temperature calibration using alumina crucible containing 1 disk of trafoperm alloy, 2 disks of nickel and 3 spikes of isotherm alloy. Aliphatic polycarbonate samples weighing 15-20 mg were used in
the alumina crucibles of volume 70 µl and heated from 30 C to 340 C at the rate of 10 C/minute and the weight of the sample with temperature is obtained. The experiment is carried out in the nitrogen and air atmosphere. The isothermal studies are done by heating the samples to a certain temperature and holding it at that temperature under the flow of air.

3.3.3. Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical relaxation measurements were made on the Rheovibron Viscoelastometer (AVD 985, Toyo Instruments), working in the tensile mode. The storage modulus E' and the loss tangent tan δ were obtained at fixed frequencies of 1 Hz, 11 Hz and 110 Hz. A temperature sweep from -160 C to maximum possible temperature was performed at the heating rate of 1 C/minute. Liquid nitrogen was used to cool the sample chamber below the sub ambient temperatures. The maximum temperature is limited by the strength of the sample, which reduces considerably after the glass transition. The specimens used were rectangular strips, approximately 3 mm wide, 0.3 mm thick and 20 mm long. A variable tension of 16-21 grams was applied to the samples. Smaller tension was required to prevent the sample from breaking before the glass transition temperature and to prevent the elongation of the sample from exceeding the maximum allowed length in the DMA sample chamber.
3.3.4. Tensile Testing

All tensile testing was done on Instron 1122 tensile tester. All tests were done in a thermally conditioned room at 23±2°C temperature and approximately 60% relative humidity using a load cell of 200 lbs. The tensile samples were cut from the polymer sheets using razors in accordance with the ASTM standard 882. The samples had a gauge length of 5 inch and width of at least 6 mm. The samples of linear pentylene PC, linear hexene PC and linear octene PC were very fragile at room temperature and they were not tensile tested. The tensile behavior of Cyclo hexene polycarbonate and the terpolymer was tested at the crosshead speed of 1 mm/min whereas polypropylene carbonate samples were tested at crosshead speeds of 1 mm/min and 50 mm/min. The tensile behavior of polyethylene carbonate was tested at the crosshead speeds of 10, 20, 50 and 100 cm/min. Minimum 5 samples of each type were tested under the given operating conditions.

3.3.5. Gel Permeation Chromatography

Gel Permeation chromatography (GPC) was performed using Waters 590 model with μ-Styragel columns in THF as solvent. The solutions of concentration of approximately 9 mg/5 ml were used. The 200-μl solution was injected in the column with flow rate of 1 ml/min at 40°C. The column was calibrated using polystyrene standards of molecular weights 240 K, 169 K, 95 K, 50 K, 17.5 K, 3.5 K under same conditions. The column measures the differential refractive index of the solvent.
3.3.6. Processibility and Rheometry

The Dynisco series 4003 melt flow indexer was used to study the melt flow index of polyethylene carbonate and the terpolymer. The studies were performed at different temperatures. At least 5 different readings were taken at each operating condition. The sample weight is measured only after the steady flow rate is established in the melt flow indexer. The melt flow index of terpolymer is measured at three temperatures: 200°C, 205°C, and 210°C. The Hitachi S-3000N electron microscope was used to observe the surface roughness of the extrudate at different temperatures in the melt flow indexer.

The paar physica MCR 300 parallel plate rheometer was used to study the rheological behavior of the polymers. The plates of radii 5 cm were used. The amplitude sweep, frequency sweep, and flow curve experiments were performed on the samples. The samples were cut from the sheets of approx 1mm thickness and pressed between the parallel plates ensuring that there is no air gap left between the plates. The polycarbonates based on linear pentene, linear hexene, and linear octene were tested at 140°C, poly (ethylene carbonate) and poly (propylene carbonate) was tested at 160°C whereas the Terpolymer and cyclo hexene polycarbonate were tested at 210°C. The temperatures were decided from the glass transition and thermal degradation studies and the melt flow index studies of the polymers. Ms. Sarla Goel from Paar Physica Inc. kindly provided the heating jacket required for higher temperatures in the case of some polymers.
Chapter 4

RESULTS AND DISCUSSIONS

4.1. Thermal Properties:
Thermal behavior of the thermoplastics is important for deciding the operating conditions during their processing. The lower end of the processing temperature is the glass transition temperature in the case of amorphous polymers and melting temperature in the case of semi-crystalline polymers. The degradation temperature decides the upper end. Also, the thermal properties are important to decide the potential applications of the polymers and the temperatures involved in those applications.

4.1.1 Glass Transition Temperature ($T_g$):
The glass-rubber transition occurs when the free volume associated with the chain increases above a certain value. The polymer turns from a glassy to a rubbery state as the polymer is heated and long-range molecular motions become possible. The glass transition temperatures of the aliphatic polycarbonates were obtained using the Differential Scanning Calorimetry (DSC). The polymers were found to be completely amorphous with no crystallite melting observed in the DSC scans. No crystal growth was observed in the optical microscopes as well. The non-crystallinity of these polymers is assigned to the irregularities formed during the polymerization.
reaction. The FTIR scans were taken for these polymers and a distinct peak around 1200-1250 cm$^{-1}$ was obtained in all polymers. This can be assigned to the ether group formed during the polymerization. The DSC scans for the aliphatic polycarbonates are shown in figures 4.1 and 4.2. The glass transitions, not being first order transitions, do not appear as peaks, but appear as changes of slope. The vertical axis represents heat capacity and a glass transition appears as a change in heat capacity, but usually spread over a range of temperature. The transition temperature is usually identified with the point of inflexion. In some cases the range over which the transition occurs is quoted as well as the point of inflexion, since the range can be affected by the crystallinity, micro structural defect content and comonomer content. The point of inflexion and the temperature range for glass transition for aliphatic polycarbonates is tabulated in table 4.1.

It is generally accepted that there is a correlation between the glass transition temperature and the chemical structure of polymers. The rationale is based on the assumption that the functional groups in the repeat unit provide weighted additive contributions to the $T_g$, although the fundamental process involves the rotational potential energy diagram of the polymer chain. It should also be noted that the polymer molecules couldn’t move or reorient without the co-operation of their intermolecular neighbors. Thus intermolecular co-operativity and the size of the smallest segmental unit of rotation (conformer) that is surrounded by other conformers in a solid state affect the glass transition temperature [22].
Figure 4.1. DSC curves for the glass transition of aliphatic polycarbonates. (Heating Rate= 10 C/min).
Figure 4.2. DSC curves for the glass transition of aliphatic polycarbonates. (Heating Rate= 10 C/min).
Table 4.1. Glass Transition Temperature range and Inflection point for aliphatic polycarbonates.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tg range (°C)</th>
<th>Tg (Inflection Point) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene carbonate</td>
<td>8 to 12</td>
<td>10</td>
</tr>
<tr>
<td>Polypropylene carbonate</td>
<td>22 to 30</td>
<td>28</td>
</tr>
<tr>
<td>Poly (linear-pentene carbonate)</td>
<td>-6 to -1</td>
<td>-4</td>
</tr>
<tr>
<td>Poly (linear-hexene carbonate)</td>
<td>-12 to -7</td>
<td>-10</td>
</tr>
<tr>
<td>Poly (linear-octene carbonate)</td>
<td>-18 to -12</td>
<td>-16</td>
</tr>
<tr>
<td>Poly (cyclohexene carbonate)</td>
<td>99 to 111</td>
<td>105</td>
</tr>
<tr>
<td>Terpolymer of CO₂, propylene oxide (20%) and cyclohexene oxide (80%)</td>
<td>89 to 100</td>
<td>97</td>
</tr>
</tbody>
</table>
From figures 41, 42 and table 41 we see that the glass transition temperature of aliphatic polycarbonates decreases as the length of the side chain in the repeat unit increases, except for the polypropylene carbonate. From the structural formulae given in equations 31 to 36 we see that the number of C-atoms in the side chain of the repeat unit increases in the homologous series of aliphatic polycarbonates from polyethylene carbonate to linear octene polycarbonate except cyclohexene polycarbonate, which has a cyclic monomer. Since the polymers are polar chains with some dipolar interactions contributing to the bonding, it appears that the longer flexible side chains are pushing the main chains apart and lowering the glass transition through that mechanism. It is also possible that the amount of dipolar bonding per unit volume is being reduced as the hydrocarbon content of the polymers increases relative to the dipolar content. Hence the glass transition decreases from +8 °C for polyethylene carbonate to −16 °C for linear octene polycarbonate. In a similar manner to that established for polyacrylates, increasing the length of the linear side chain does not increase the glass transition, but decreases it. This process is known as internal plasticization. The glass transition temperatures are plotted against the length of side chain in figure 43.

The glass transition temperature increases from polyethylene carbonate to polypropylene carbonate, in a similar manner from polyethylene and polypropylene. The CH₃ side group in the latter is bulkier than the H group in the former, close to the chain and directly increases the activation energy for rotation about the
Figure 4.3. Glass transition temperatures of aliphatic polycarbonates against the number of carbon atoms in the side chain of the repeat unit.
backbone Hence it increases the glass transition temperature by increasing the barrier for the molecular motions. The aliphatic polycarbonates with the bulky group in the main chain, i.e., cyclohexene polycarbonate and the terpolymer, have a higher glass transition temperatures than the other samples viz. +104°C and 97°C respectively.

4.1.2. Thermal Degradation:

The thermal degradation of the polymers was studied in the DSC by heating the polymer at 10°C/min till the polymer degrades. The degradation was identified as a peak in the DSC scans. The combined DSC scans for the degradation studies are as shown in Figure 44. The continuous flow of nitrogen was maintained in DSC. Thermo gravimetric analysis (TGA) was also used to study the degradation temperatures. The TGA curves for the samples under the air and nitrogen atmospheres are given in figures 45 to 411.

It can be seen that the aliphatic polycarbonates undergo thermal degradation at considerable lower temperatures than chain reaction polymers such as PE and PP. It can also be seen that the thermal degradation occurs at higher temperatures in the nitrogen atmosphere than in air. This suggests that oxidation may be one of the important mechanisms responsible for the degradation of the aliphatic polycarbonates. Although the thermal degradation of the polymers cannot be eliminated completely during the processing of polymers, it must be held to a
Figure 4.4. DSC curves for the thermal degradation of aliphatic polycarbonates. (Heating Rate= 10 C/ min)
Figure 4.5. TGA curves for thermal degradation of polyethylene carbonate in air and nitrogen atmospheres
Figure 4.6. TGA curves for thermal degradation of polypropylene carbonate in air and nitrogen atmospheres
Figure 4.7. TGA curves for thermal degradation of linear pentene polycarbonate in air and nitrogen atmospheres
Figure 4.8. TGA curves for thermal degradation of linear hexene polycarbonate in air and nitrogen atmospheres.
Figure 4.9. TGA curves for thermal degradation of linear octene polycarbonate in air and nitrogen atmospheres
Figure 4.10. TGA curves for thermal degradation of the Terpolymer of propylene oxide, cyclohexene oxide and carbon dioxide in air and nitrogen atmospheres.
Figure 4.11. TGA curves for thermal degradation of cyclohexene polycarbonate in air and nitrogen atmosphere.
minimum to keep the quality of the final products high. The degradation studies will enable us to determine the optimum operating conditions for the processing of these polymers. In the TGA curves the temperature at which the polymer starts to degrade and polymer weight starts decreasing rapidly is called the initial decomposition temperature (IDT). The DSC degradation peak temperatures, initial decomposition temperatures in the presence of air and nitrogen atmospheres and percentage weight of the samples remaining after the degradation are tabulated in table 4.2. It can be seen that the degradation temperature of aliphatic polycarbonates increases with the increasing hydrocarbon content in the polymer. The plot of IDT (air) against the hydrocarbon content of the repeat unit of the polymer is shown in figure 4.12.

Thus, the chemical structure of the polymer not only affected the glass transition but also the degradation temperature. This fact is important in the sense that it would decide the processing temperature window for the given polymer depending on its $T_g$ and IDT, which further depend on its structure. Figure 4.13 plots (IDT-$T_g$) versus $T_g$ for aliphatic polycarbonates.

4.1.3. Isothermal studies:

Isothermal degradation studies were also performed on aliphatic polycarbonates using DSC and TGA. The polymers were raised to a certain temperature and held for 30 minutes at that temperature. In TGA the weight of the sample was recorded while in DSC the heat supplied to the sample is recorded. It was found that the weight of
Table 4.2. DSC degradation temperature and IDT for aliphatic polycarbonates.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>DSC Peak Temperature (C)</th>
<th>IDT (Air) (C)</th>
<th>IDT (Nitrogen) (C)</th>
<th>% Weight of Sample remaining (DSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene carbonate</td>
<td>229</td>
<td>217</td>
<td>232</td>
<td>7.1</td>
</tr>
<tr>
<td>Polypropylene carbonate</td>
<td>253</td>
<td>235</td>
<td>238</td>
<td>4.5</td>
</tr>
<tr>
<td>Poly (linear pentene carbonate)</td>
<td>283</td>
<td>246</td>
<td>270</td>
<td>2.65</td>
</tr>
<tr>
<td>Poly (linear hexene carbonate)</td>
<td>290</td>
<td>250</td>
<td>280</td>
<td>2.43</td>
</tr>
<tr>
<td>Poly (linear octene carbonate)</td>
<td>295</td>
<td>257</td>
<td>268</td>
<td>5.66</td>
</tr>
<tr>
<td>Poly (cyclo hexene carbonate)</td>
<td>308</td>
<td>282</td>
<td>290</td>
<td>4.27</td>
</tr>
<tr>
<td>Terpolymer of CO2, propylene oxide (20%) and cyclohexene oxide (80%)</td>
<td>296</td>
<td>265</td>
<td>276</td>
<td>0.074</td>
</tr>
</tbody>
</table>
Figure 4.12. IDT in air plotted against the hydrocarbon content in aliphatic polycarbonates.
Figure 4.13. \((\text{IDT}-T_g)\) plotted against \(T_g\) for aliphatic polycarbonates.

\[
y = -4E-05x^3 + 0.0138x^2 - 1.6001x + 241.98
\]
the samples remains well above 98% of the initial weight in TGA and the heat supplied to the samples remain fairly constant within the experimental results in DSC. This suggests that the samples are thermally stable at the testing temperatures as shown in figures 4.14 and 4.15.

4.2. Dynamic Mechanical Analysis:

The Dynamic Mechanical Analyzer is designed to impose a sinusoidal strain, in tension, on the sample and to measure the sinusoidal stress response of the material with respect to amplitude and phase. The tangent of the phase angle existing between the sinusoidal deformation and the stress response of the sample represents the damping factor or mechanical loss tangent (tan δ) of the sample. The amplitude of the sinusoidal deformation is kept small (approx. $1 \times 10^{-3}$ cm i.e. 0.03 to 0.05 % strain) to insure linear viscoelastic response.

4.2.1. Glass transition temperature:

The transitions in the polymers can be depicted as the peaks in the tan δ curves at the given frequency. The mechanical loss tangents of the aliphatic polycarbonates obtained from DMA measurements at 1 Hz are shown in figure 4.16. It can be seen that for all samples of aliphatic polycarbonates single, well-defined transition is obtained. The trend of the $T_g$ along the series of aliphatic polycarbonates remains the
Figure 4.14. Isothermal DSC runs for aliphatic polycarbonates
Figure 4.15. Isothermal TGA curves for aliphatic polycarbonates
Figure 4.16. Tan $\delta$ for the series of aliphatic polycarbonates at 1.1 Hz
same as observed in DSC, however, the $T_g$ obtained from DMA is larger than that obtained from DSC. Dutt [59] has also obtained very similar results. The difference is reasonable in the view of the tensile strain applied to the samples in the DMA, at the frequency of 1.1 Hz, simultaneously with the rate of temperature sweep. The thermocouple in the sample chamber is positioned near the sample so that the temperature was within ±1°C of the required temperature.

The Autovibron Dynamic Viscoelastometer used in this study cycled each sample at a specific temperature 10 times. Each cycle allowed for collection of 40 points per cycle and therefore 400 points were collected at each particular temperature and frequency. This reduces the random error associated with each data point by the factor of square root of the number of points collected. As a result, the points used to plot the curves are larger than the error bars.

4.2.2 Frequency dependence of dynamic-mechanical properties:

The graphs of tan δ vs temperature at different frequencies are plotted in figures 4.17 to 4.23. It can be seen that the glass transition temperatures (the peaks of tan δ curves) increase with frequency of mechanical deformation of polymer. The glass transition temperatures, as obtained from the peaks of tan δ curves are tabulated in table 4.3. In the polymer, the thermal transition occurs when the time required for the relaxation equals the time scale of the experiment at that temperature.
Figure 4.17. DMA loss tangent (tan δ) for polyethylene carbonate at different frequencies.
Figure 4.18. DMA loss tangent (tan $\delta$) for polypropylene carbonate at different frequencies.
Figure 4.19. DMA loss tangent (tan δ) for linear pentene polycarbonate at different frequencies.
Figure 4.20. DMA loss tangent (tan δ) for linear hexene polycarbonate at different frequencies
Figure 4.21. DMA loss tangent (tan δ) for linear octene polycarbonate at different frequencies.
Figure 4.22. DMA loss tangent (tan δ) for terpolymer of CO₂, propylene oxide and cyclo hexene oxide at different frequencies.
Figure 4.23. DMA loss tangent ($\tan \delta$) for cyclo hexene polycarbonate at different frequencies.
Table 4.3. Glass transition temperatures obtained from DMA for aliphatic polycarbonates at different frequencies.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Glass Transition Temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.1 Hz</td>
</tr>
<tr>
<td>Polyethylene carbonate</td>
<td>191</td>
</tr>
<tr>
<td>Polypropylene carbonate</td>
<td>43.4</td>
</tr>
<tr>
<td>Poly (linear pentene carbonate)</td>
<td>12.4</td>
</tr>
<tr>
<td>Poly (linear hexene carbonate)</td>
<td>5.6</td>
</tr>
<tr>
<td>Poly (linear octene carbonate)</td>
<td>1.2</td>
</tr>
<tr>
<td>Poly (cyclo hexene carbonate)</td>
<td>136.6</td>
</tr>
<tr>
<td>Terpolymer of CO2, propylene oxide (20%) and cyclohexene oxide (80%)</td>
<td>119.6</td>
</tr>
</tbody>
</table>
Hence depending upon the relaxation theory of glass transition we can conclude that the same polymer will undergo a certain transition at a higher temperature when the frequency of deformation is increased or time scale of the experiment is decreased. The glass transition temperature of the terpolymer is between cyclohexene polycarbonate and polypropylene carbonate and we found it close to that predicted on a rule of mixtures basis at all frequencies as shown in appendix 2. This suggests that random copolymers can be synthesized to have specific designed glass transition temperatures.

The dependence of $T_g$ on frequency throws light on the relaxation mechanism of the polymer chains during the transition and gives the activation energy of the glass transition for the polymer as given by the Arrhenius equation

$$\log(f) = A + \left( \frac{-\Delta E}{2 \times 303RT_g} \right)$$

(4.1)

Where, $f$ - Frequency of the applied signal

$\Delta E$ - Activation energy of the relaxation process

$R$ - Universal gas constant

$T_g$ - Glass transition temperature

The entropy of polymeric relaxation process at each frequency is obtained using the formula

$$\Delta E = RT_g \left[ 1 + \ln \left( \frac{k}{2\pi \hbar} \right) + \ln \left( \frac{T_g}{f} \right) \right] + T_g \Delta S$$

(4.2)
Where, $k$-Boltzmann’s constant

$h$-Planck’s constant

$\Delta S$-Activation entropy of the relaxation process

$\Delta E$ and $\Delta S$ for the aliphatic polycarbonates are tabulated in table 4.4. $\Delta E$ for aliphatic polycarbonates is plotted against $T_g$ and the length of the side chain in figures 4.24 and 4.25. It can be seen that the activation energy initially increases from polyethylene carbonate to polypropylene carbonate due to introduction of the $-\text{CH}_3$ group. $\Delta E$ decreases with the increase in the length of flexible side chain i.e., from polypropylene carbonate to linear pentene polycarbonate, which means that the flexible side chain has made the long-range conformational changes easier in the main chain. However as the length of the side chain increases from linear pentene polycarbonate to linear octene polycarbonate the energy of activation increases. This is because the side chain might fall back on itself and makes the conformational changes in the main chain difficult. However since the longer side chain pushes the dipolar polymer chains apart the $T_g$ in fact decreases however the energy of activation increases. Hence linear octene polycarbonate has higher activation energy than other polycarbonates. The terpolymer (7) and cyclo hexene polycarbonate also have high $\Delta E$ due the presence of stiff cyclo hexene ring in the main chain. As already mentioned the error in measurement of $\Delta E$ causes the error in determination of $\Delta S$, as the errors due to temperature and frequency are negligibly small. $\Delta S$ follows the same trend as $\Delta E$ as shown in figure 4.26.
Table 4.4. Activation energies and Activation entropies of Glass transition process of aliphatic polycarbonates obtained from DMA.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Activation Energy (KJ/mol)</th>
<th>Activation Entropy at 1.1 Hz (J/mol/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene carbonate</td>
<td>288.6</td>
<td>751</td>
</tr>
<tr>
<td>Polypropylene carbonate</td>
<td>290.0</td>
<td>679</td>
</tr>
<tr>
<td>Poly (linear pentene carbonate)</td>
<td>233.6</td>
<td>581</td>
</tr>
<tr>
<td>Poly (linear hexene carbonate)</td>
<td>267.1</td>
<td>722</td>
</tr>
<tr>
<td>Poly (linear octene carbonate)</td>
<td>368.9</td>
<td>1108</td>
</tr>
<tr>
<td>Poly (cyclo hexene carbonate)</td>
<td>366.2</td>
<td>654</td>
</tr>
<tr>
<td>Terpolymer of CO₂, propylene oxide (20%) and cyclohexene oxide (80%)</td>
<td>336.4</td>
<td>617</td>
</tr>
</tbody>
</table>
Figure 4.24. Activation Energy vs. length of Side chain in aliphatic polycarbonates
Figure 4.25. Activation energy vs. glass transition temperature for aliphatic polycarbonates.
Figure 4.26. Activation Entropy vs. Side chain length at different frequencies for aliphatic polycarbonates
4.2.3. **Dynamic Mechanical Spectrum:**

The dynamic mechanical spectra for the polymers in which the elastic storage and loss modulus is plotted vs temperature are given from figures 427 to 433. However, there is error in the absolute values of the storage and loss modulus caused due to inaccurate measurement of the cross sectional area of the samples. Especially in the case of polymers that have sub-zero glass transition temperature, the polymer films are very delicate. Small error in the cross sectional area changes the moduli to a greater extent in the case of thin films. Also, the thermal expansion and contraction of the sample is to be taken into account over such a large temperature range. Hence, we are not comparing the actual values of the elastic storage and loss moduli and the peak of tan δ obtained from DMA. Nevertheless, we observe drastic decrease in storage modulus and peaks in loss modulus and tan δ at the glass transition temperature. Since there is negligible error in the measurement of frequency and temperature, we studied the frequency dependence of glass transition temperature.

The frequency dependence of the glass transition temperature is also evident from the dynamic mechanical relaxation spectra. It is interesting to see from the dynamic relaxation spectra and also from the tan δ curves that there is no substantial evidence of secondary transition in aliphatic polycarbonates as such from DMA. In some cases (especially in the case of polypropylene carbonate) we have obtained peaks in
Figure 4.27. Dynamic mechanical spectra for polyethylene carbonate at different frequencies.
Figure 4.28. Dynamic mechanical relaxation spectra for polypropylene carbonate at different frequencies
Figure 4.29. Dynamic mechanical relaxation Spectra for linear pentene polycarbonate at different frequencies.
Figure 4.30. Dynamic Mechanical relaxation spectra for linear hexene polycarbonate at different frequencies
Figure 4.31. Dynamic mechanical relaxation spectra for linear octene polycarbonate at different frequencies.
Figure 4.32. Dynamic mechanical relaxation spectra for terpolymer at different frequencies
Figure 4.33. Dynamic Mechanical relaxation spectra for cyclo hexene polycarbonate at different frequencies
loss modulus below $T_g$ around $-70^\circ C$ (figures 4 18 and 4 278), which we consider to be the secondary transition in polypropylene carbonate.

In the dynamic relaxation spectra of cyclohexene polycarbonate and the terpolymer, the graph of $E'$ vs. Temperature contains a small shoulder. No evidence of crystallization is observed during the temperature sweep in DSC and also using the optical microscopy. The shoulder in the $E'$ can be assigned to the flipping of the disubstituted cyclohexane ring present in the polymer molecules. Since one of the sides of the ring is a part of the main chain, it is obvious that the cyclohexene ring flips from one chair conformation to other by axial-equatorial mechanism simultaneously during the glass transition, when the main chain undergoes long-range conformational changes. This can be corroborated by the fact that the shoulder is obtained just during the glass transition of these two polymers.

This phenomenon is also observed in polycyclohexyl methacrylate in which the flip mechanism of the cyclohexane group, which is in the side branch of the main polymer chain, gives rise to a low temperature secondary peak [7] when the polymer backbone remains fixed in position.
4.3. Mechanical Properties:

The macroscopic fracture behavior of the polymers is often described in terms of being ductile or brittle. Although highly desirable, such behavior is difficult, if not impossible, to correlate with the molecular structure or relaxation processes in the polymers because the macroscopic ductility or brittleness of any material is affected by the complex interactions between many external factors such as the state of the stress applied, the rate of deformation, the temperature, etc and material and specimen factors such as the specimen geometry, the amount and severity of flaws, the crystalline morphology, the thermal history, the presence of additives etc. In the case of polymers the molecular weight and its distribution and the cross-link density is also important. Notwithstanding these complex factors, meaningful correlation can still be obtained using carefully controlled test and sample conditions [61].

Many researchers [62, 63] have attempted to correlate the secondary relaxation with the large strain properties of the polymers usually in the terms of activation energies. However such relationships are more suggestive than substantial [61]. Firstly the dynamic mechanical measurements are made in linear viscoelastic region while the plastic deformation and fracture occurs at much larger strain. Moreover the dynamic mechanical analysis doesn't take into account the nature and extent of intermolecular interactions beyond allowing one to compare the apparent activation energies of relaxation in the homologues. In large-scale deformation, there is no doubt that intermolecular interactions would come into play.
In the case of aliphatic polycarbonates it was found that the polymers linear pentene polycarbonate, linear hexene polycarbonate and linear octene polycarbonate which have $T_g$ in the subzero region are mechanically very delicate at room temperature. The films prepared from these samples were so weak and flimsy that tensile testing on those films was not conducted. These polymers will have applications not based on their mechanical properties but because of other properties such as processibility and thermal degradation. The tensile properties of remaining polymers viz. polyethylene carbonate, polypropylene carbonate, cyclohexene polycarbonate and the terpolymer were determined at room temperature.

The representative engineering stress-strain curves for cyclohexene polycarbonate, terpolymer and polypropylene carbonate are shown in figure 4.34. The crosshead speed used for terpolymer and cyclohexene polycarbonate is 1 mm/min while for polypropylene carbonate is 10 mm/min. It can be seen that the mechanical properties of the polymers are related to the $T_g$, which is further related to structure of the polymers. The elastic modulus of the polymers decrease from cyclohexene polycarbonate to terpolymer to polypropylene carbonate in the same order as their $T_g$. Cyclohexene polycarbonate and the terpolymer behave as brittle material at room temperature and their strain at break is obtained to be less than 1%. The tensile strengths for cyclohexene polycarbonate and the terpolymer are very close,
Figure 4.34. Representative stress-strain curves for aliphatic polycarbonates.
however there is a marked increase in the modulus and decrease in strain at break from terpolymer to cyclohexene polycarbonate. The reason for this is again the reduction in the chain stiffness in the molecules of former due to incorporation of 20% polypropylene oxide during synthesis. Thus we observe that incorporation of the flexible units in main chain of polymer causes plasticization as was caused by the flexible side chains in the other homologues of aliphatic polycarbonates.

The plots of tensile strength vs. strain at break and modulus vs strain at break are shown in figures 4.35 and 4.36 respectively. It can be seen that polypropylene carbonate, although tested at higher crosshead speed, has smaller modulus, tensile strength and higher strain at break as compared to the terpolymer and cyclohexene polycarbonate. It is important to note that the propylene polymer shows a very clear yield behavior at high strains and exhibits toughness, which can be identified with the area under the curve to fracture. Of the three polymers it has the greatest potential for exhibiting fracture toughness as does the aromatic polymer in common use.

Poly (ethylene carbonate) with glass transition temperature 8°C shows rubbery mechanical behavior at room temperature. Poly (ethylene carbonate) was tested at the crosshead speeds of 10, 20, 50 and 100 cm/min and the stress-strain curves are showing typical rubber elasticity as shown in figure 4.37. It is seen that the polymer
Figure 4.35. Tensile strength vs. strain at break for aliphatic polycarbonates.
Figure 4.36. Elastic modulus vs. strain at break for aliphatic polycarbonates
Figure 4.37. Representative stress-strain curves for polyethylene carbonate at different crosshead speeds.
doesn’t break even after 600 % strains where we reach the limits of the instron machine to further elongate the sample. There is evidence for strain hardening at high strains, which is usually associated with crystallization under stress only at higher strain rates. Another important thing we found is that there is no tensile set in the samples of polyethylene carbonate, indicating remarkably good rubber elastic behavior without crosslinking. It therefore has considerable potential for use as an elastomer, which can be environmentally degraded. The effect of strain rate on modulus of polyethylene carbonate is shown in figure 438. The modulus increases from 3 MPa to 8 MPa with the increase in the crosshead speed from 10 cm/min to 100 cm/min.

Thus at room temperature the aliphatic polycarbonates which are below their glass transition temperatures undergo brittle failure at strains of 7-8% % for polypropylene carbonate, 0.7-0.8 % for the terpolymer and 0.5-0.6 % for cyclohexene polycarbonate whereas polyethylene carbonate which is above its glass transition temperature shows rubber elasticity with more than 600 % strain at break, that too at higher strain rates.

We have performed the statistical analysis of the strain rate dependence of the modulus of polyethylene carbonate in appendix 3.
Figure 4.38. Elastic modulus vs. crosshead speed for polyethylene carbonate.
The effect of operating temperature (and strain rate in some cases) on the mechanical properties of the materials were not studied in this project, but would be needed for a more complete evaluation of the potential uses of these materials. The room temperature average mechanical properties for aliphatic polycarbonates are tabulated in Table 4.5.

4.4. Processibility and Rheology:

4.4.1. Melt Flow Index:

It is reported that the processing temperature for poly(ethylene carbonate) and poly(propylene carbonate) is 150°C [42]. The Melt Flow Index (MFI) studies were done on poly(ethylene carbonate) and the terpolymer samples, which were available in significant amounts. The load of 216 Kg was used in all studies. At 150°C, the polyethylene carbonate extrudate surface was not smooth; the MFI was determined at 165°C to be 10.83 grams/10 minutes according to ASTM standard 1238.

The MFI for the terpolymer was determined at three temperatures. At 200°C, the extrudate surface was not smooth with stick-slip phenomena occurring in the die. Obviously, the polymer was not processible at that temperature. The MFI studies were carried out at 205 and 210°C. Relatively smooth extrudate was obtained at 210°C. The MFI at 205°C was found to be 1.55 g/10 min while at 210°C, MFI was found...
Table 4.5. Average mechanical properties of aliphatic polycarbonates.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Modulus (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Strain at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene carbonate</td>
<td>3-8</td>
<td>-</td>
<td>&gt;600</td>
</tr>
<tr>
<td>Polypropylene carbonate</td>
<td>212</td>
<td>9</td>
<td>8</td>
</tr>
<tr>
<td>Terpolymer of CO2, propylene oxide (20%) and cyclohexene oxide (80%)</td>
<td>2080</td>
<td>13.5</td>
<td>0.7</td>
</tr>
<tr>
<td>Poly (cyclohexene carbonate)</td>
<td>2460</td>
<td>11.8</td>
<td>0.5</td>
</tr>
</tbody>
</table>
to be 3.264 g/10 min. The SEM micrographs for the surface of the extrudate obtained from melt flow indexer are as shown in figure 4.39 a to c. These micrographs are taken at the same magnification. SEM was used to obtain the depth of focus over the entire sample thickness. Thus we see that the terpolymer is not processible below 210°C. Similar studies can be done on other samples of aliphatic polycarbonates. The surface roughness of the samples can also be quantified.

4.4.2. Rheometric Studies:

Melt Index or fluidity index provides a single point (shear rate) measurement of the flowability of the material. Sometimes high load melt index (HLMI) is also determined using the load of 10 kg in Melt flow indexer. This single point value is a composite of both viscosity and elasticity of the sample and it is not possible to determine the effect of viscosity contribution independent from the elasticity. For characterizing and comparing materials the measurement of well defined rheological material properties provide a more reliable basis.

Rheological measurements are of practical importance whether we are involved in manufacturing the resin, producing machinery used in resin production or processing the resin into a final product. These quantitative, objective measurements bridge the gap between the molecular structure, processibility and ultimate performance properties. In rheometry we evaluate and understand the complex flow characteristics of polymers over wide range of deformation conditions and also
Figure 4.39. SEM micrographs of the surface roughness of the extrudate of terpolymer at different temperatures; a) 200°C  b) 205°C  c) 210°C.
discover how the elastic and viscous components contribute to the overall flow properties

Rheometer controls three parameters in any given test frequency of oscillation, amplitude of oscillation, and test temperature. A typical test holds two of these parameters constant while varying the third. In a frequency sweep (a sweep is a continuous variation of a parameter) the test frequency is varied to establish the frequency dependence of a material. One example of such dependence is shear thinning, or the change in viscosity or elasticity as a function of frequency. Strain or amplitude sweeps are used to measure the range of linear viscoelastic behavior of materials. The shear moduli of a material are independent of strain amplitude up to a certain applied strain. Within such a range they are said to be linearly viscoelastic. Beyond that point the structure of the material begins to break down and the elastic modulus drops.

4.4.2.1. Shear Thinning behavior:

Non-Newtonian shear thinning behavior of the polymer is studied by the change in viscosity against the shear rate. Varying the frequency of rotation of the parallel plate varies the shear rate.

Before studying shear-thinning behavior, gel permeation chromatography was used to find the molecular mass distribution of aliphatic polycarbonates and the combined curves are given in figure 4.40. Although the absolute values of the molecular
Figure 4.40. GPC curves for aliphatic polycarbonates
weights cannot be obtained just by using GPC the polystyrene equivalents of the molecular weights are tabulated in table 4.6. It can be seen from the GPC curves that linear pentylene, hexene and octene polycarbonates do not have a normal distribution of the molecular weight. It is found that the solutions of these polymers in THF are stable with no precipitation occurring after solution is allowed to stand for 7 days. Polyethylene carbonate is found to be insoluble in THF and hence its MMD is not obtained.

From the GPC curves for linear pentene, hexene and octene polycarbonates we see that these polymers have a significant population of the high molecular weight molecules. There is also a considerable population of low molecular weight molecules and the distribution tends to be bimodal and broad. The molecular mass for the other for remaining polymers show normal and narrow distribution.

The apparent viscosity of aliphatic polycarbonates is plotted against the shear rate in figure 4.41. These curves are called flow curves of the polymers. It has to be noted that since the processing temperatures of aliphatic polycarbonates are different the flow curves for these polymers are obtained at their processing temperatures. Linear pentylene, hexene and octene polycarbonates are tested at 140°C, polyethylene carbonate was tested at 150°C, polypropylene carbonate at 180°C while terpolymer and cyclohexene polycarbonate were tested at 210°C. Although for comparison
Table 4.6. Polystyrene equivalent molecular weights of aliphatic polycarbonates.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( M_W )</th>
<th>( M_N )</th>
<th>PDI (Polydispersity Index)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene carbonate</td>
<td>28900</td>
<td>7540</td>
<td>3.83</td>
</tr>
<tr>
<td>Linear pentene polycarbonate</td>
<td>44400</td>
<td>7500</td>
<td>5.13</td>
</tr>
<tr>
<td>Linear hexene polycarbonate</td>
<td>45500</td>
<td>9490</td>
<td>4.79</td>
</tr>
<tr>
<td>Linear octene polycarbonate</td>
<td>49400</td>
<td>10500</td>
<td>4.70</td>
</tr>
<tr>
<td>Terpolymer of CO2, propylene oxide (20%) and cyclohexene oxide (80%)</td>
<td>35200</td>
<td>8680</td>
<td>5.27</td>
</tr>
<tr>
<td>Poly (cyclo hexene carbonate)</td>
<td>33800</td>
<td>7980</td>
<td>4.23</td>
</tr>
</tbody>
</table>
Figure 4.41. Flow curves for aliphatic polycarbonates
purposes the flow curves for the polymers should be obtained at the same temperature, we assume that the activation energy is not the function of shear rate for these polymers in the given temperature range and the shape of flow curve will not change drastically with temperature.

From figure 4.41, we observe that polyethylene carbonate and polypropylene carbonate show highly shear thinning behavior. Moreover their critical shear rate at which the shear thinning starts is large as compared to other polymers. Polyethylene carbonate shear thins to a very low viscosity at higher shear rates. It is confirmed that there is no mechanical degradation occurring in the polymer because we observed the recovery of the viscosity at the lower shear rates in the same polymer sample. This extremely high shear thinning behavior of polyethylene carbonate and polypropylene carbonate is of great advantage in high shear processes like injection molding and extrusion.

This high degree of shear thinning is supposed to be because of breakdown of strong secondary intermolecular bonds existing in polar molecules at higher shear rates. Polyethylene carbonate and polypropylene carbonate have small pendant side chains in the repeat unit and hence can have strong intermolecular bonds. These bonds are broken down due to high shear and the viscosity of the polymers decreases drastically after certain shear rate. As the length of the side chain increases the
intermolecular interactions are hindered and the molecules are pushed apart. Thus molecules can slip past one another and cause shear thinning at lower shear rates.

In the case of cyclohexene polycarbonate and the terpolymer, although the molecular weight distribution is similar to that of polypropylene carbonate the flow curves are different due to the effect of bulky cyclohexene group in the main chain. As expected, the terpolymer flow properties (such as onset of shear thinning, zero shear viscosity) fall in between cyclohexene carbonate and polypropylene carbonate as shown by separate flow curves in figure 4.42. Due to high $T_g$, the processing temperatures for cyclohexene polycarbonate and terpolymer are higher than other aliphatic polycarbonates. Even at the highest testing temperatures these two polymers show highest zero shear viscosity due to stiff polymer chains.

In the case of linear pentene, hexene and octene polycarbonates in addition to the effect of longer side chains we have to also consider the effect of MMD. In these polymers even though the side chains contain merely 3,4,6 C-atoms, due to the alternating co-polymerization, each repeat unit will have a side chain and hence the effect of these side chains on hindering the intermolecular dipolar interactions will be considerable. In addition to that these polymers have a significant population of high molecular weight molecules which gives rise to non-Newtonian behavior at lower shear rates as explained earlier. This can be observed in figure 4.41. The shear rate corresponding to the onset of shear thinning increases from linear octene.
Figure 4.42. Flow curves for polypropylene carbonate, cyclohexene polycarbonate and the terpolymer.
polycarbonate to linear hexene polycarbonate to linear pentylene polycarbonate

However there is no significant difference in the rate of shear thinning in these three polymers. These polymers do not undergo high shear thinning as polyethylene carbonate and polypropylene carbonate because of presence of high molecular weight molecules, which dominates the rheological behavior at higher shear rates.

4.4.2.2. Viscoelastic properties:

The viscoelastic properties of polymers were obtained in the dynamic oscillatory mode of the rheometer. First of all the range of strain or amplitude for the linear viscoelastic behavior of the polymer was ascertained using the amplitude or strain sweep. After choosing a certain strain in the linear viscoelastic region of the polymer we performed frequency sweep in which we varied the frequency of oscillation at constant amplitude. The plots of $G'$, $G''$ and complex viscosity $|\eta^*|$ are shown in figure 4.43. Consideration of the dynamic characteristics of the polymer melts enables us to classify their relaxation states at the temperatures above $T_g$. The region of low frequency corresponds to the fluid state, the plateau region of $G'$ ($\omega$) corresponds to the rubber-like state of linear polymers where they are not able to flow and the transition from one state to other takes place when crossover of $G'$ ($\omega$) and $G''$($\omega$) takes place. At still higher frequencies there takes place transition to the glassy state of the polymer. The dynamic method of studying the relaxation properties of polymers makes it possible to determine the frequency regions.
Figure 4.43. Experimental dependences of the components of dynamic shear modulus and complex viscosity on frequency. ($G'$ and $G''$ are in Pa; $\eta^*$ is in Pa·S)
Figure 4.43. Continued.

e) Linear octene polycarbonate

f) Terpolymer

g) Cyclohexene polycarbonate
corresponding to the transition of the polymers from the fluid state to rubbery, leathery and glassy states. The transition frequencies increase with the increase in temperature for the given polymer. The structure of the polymer affects the entanglements, which further affect the dynamic relaxation and viscoelastic properties of the polymeric chains. When the elements forming the fluctuating entanglements network are subjected to mechanical action, the most important parameter is the average lifetime of a junction or the relaxation time. If the relaxation time is very short, the structural units appear to be absolutely non-linked, they slip freely at the junctions and the system behaves as a typical liquid. If the time is infinitely long, the polymer is capable of retaining strains and stresses for an infinitely long time.

In aliphatic polycarbonates, the highly shear thinning polymers polyethylene carbonate and polypropylene carbonate show higher relaxation frequency or lower relaxation time for fluid to rubbery transition. The sub-zero glass transition polymers linear pentene, linear hexene, and linear octene polycarbonates show higher relaxation times. In a polydisperse system, we have to consider the effect of each fraction of the molecular weight on the relaxation time. These polymers have a significant population of high molecular weight molecules, which dominate the rheological properties and lead to higher relaxation times. Also, the lower testing temperature gives rise to lower relaxation frequency.
In the case of stiff polymers such as cyclohexene polycarbonate and the terpolymer, we obtain high relaxation times. The relaxation frequency of cyclohexene polycarbonate was lower than 0.1 s\(^{-1}\) and the polymer is in the elastic region over the entire frequency range (0.1-100 s\(^{-1}\)) is in the elastic region. This is important because the polymer is tested at 210 C i.e. the maximum temperature in this series and still it has highest relaxation time. The reason for lowest relaxation times for polyethylene carbonate and polypropylene carbonate which means that the chains are non-linked and slip freely at the junctions is not clearly understood.

The individual plots of \(G'\), \(G''\) and ln\(\eta\) for all the polymers are shown in figures 4.44 to 4.46. From these curves it is clear that the rheological behavior of given samples of aliphatic polycarbonates can be divided into three categories. Polyethylene carbonate and polypropylene carbonate form one group, which show high shear thinning behavior and low relaxation times. Addition of the longer side chains gives rise to another group of polymers comprising linear pentene, linear hexene and linear octene polycarbonates. This group shows lower steady state viscosities and critical shear rates due to presence of side chains, however due to the presence of significant population of high molecular weight molecules they show comparatively less shear thinning behavior and higher relaxation times. The third group consists of cyclohexene polycarbonate and the terpolymer, which show high steady state viscosities and high relaxation times due to stiff polymer chains.
Fig. 4.44.  $G'$ vs. frequency for aliphatic polycarbonates.
Figure 4.45. $G''$ vs. frequency for aliphatic polycarbonates
Figure 4.46. Magnitude of Complex Viscosity vs. frequency for aliphatic polycarbonates
Chapter 5

CONCLUSIONS AND FUTURE WORK

5.1. Conclusions:

In this study the characterization of the structure-property relationships in the family of aliphatic polycarbonates homologues is established. In general, strong correlations between the chemical structure and the thermal, mechanical, viscoelastic and rheological properties of the polymers have been identified. Specifically, it can be concluded that

1) The glass transition temperatures ($T_g$) of aliphatic polycarbonates increase with the increase in the chain stiffness. The inclusion of the side chain in the monomers increases the free volume associated with the chain and also pushes the polar polymer chains apart causing decrease in the glass transition temperature. The range of $T_g$ obtained is from $-18\,^\circ C$ for linear octene polycarbonate to $105\,^\circ C$ for cyclohexene polycarbonate. This range, which is close to the ambient, gives rise to various possible applications for aliphatic polycarbonates. The fact that the copolymer of propylene oxide and cyclohexene oxide had the glass transition that was close to that predicted on a rule of mixture basis, suggests that random copolymers can be synthesized to have tailored glass transition either side of the ambient. Such polymers could have potential use in medical and biomedical industries. For instance, the material can be designed for use in making casts or
splints, which could be applied at the temperature that does not harm the skin or tissue but which sets solid on cooling to ambient. They could also be used as switching devices, operating at specific temperature, going from glassy to rubbery in the space of few degrees

2) The thermal degradation temperatures of the polymers depend on the relative carbon monoxide content. As the carbon monoxide content in the polymers decreases the degradation temperature increases. The thermolytic behavior of aliphatic polycarbonates is unique, they show complete stability below a certain critical decomposition temperature and exhibit a near instantaneous and almost complete de-polymerization above that temperature. The decomposition temperature for aliphatic polycarbonates in air varies from 217°C for polyethylene carbonate to 282°C for cyclohexene polycarbonate. This complete burnout with negligible ash or carbon residue at relatively lower temperatures makes these polymers useful as binders, polymer foaming agents and in lost foam castings.

3) None of the polymers was found to be crystalline. It therefore appears that the catalyst system used generates micro structural defects, which inhibit crystallization. The tensile properties of aliphatic polycarbonates are also function of their chemical structure. Cyclo hexene polycarbonate and the terpolymer are brittle at room temperature while polypropylene carbonate is ductile and undergoes plastic deformation. Polyethylene carbonate is rubbery material, which
elongates to more than 600 % strain without failure. These polymers have mechanical properties for commercial usage. The polymers can be designed to use as rubbery materials such as artificial skin. The biodegradability of the polymers will enable us to design a material that would slowly degrade away in the atmosphere with regular washing. They also have potential for use in the electronics industry as leachable masks and coatings. There are many potential uses in the agricultural field for the rubbery materials. They have potential use in polymer-ceramic composites, as temporary reinforcement for brittle ceramic components. These polymers have already found applications as thermoplastic elastomers and in modifying mechanical properties of SBR after curing.

4) The processing behavior of these polymers was studied using rheometry. The melt flow index was used to find the processibility of terpolymer at various temperatures. The stick-slip phenomenon was observed at 200 °C while relatively smooth surface of the extrudate was obtained at 210 °C. All the polymers were found to be shear thinning. Polypropylene carbonate and polyethylene carbonate were found to be highly shear thinning, however the onset of shear thinning in both the polymers was after shear rate was greater than 1 s⁻¹. This shear thinning behavior with small viscosities at higher shear rates makes polyethylene carbonate and polypropylene carbonate as ideal candidates for injection molding and extrusion operations. Linear pentylene, linear hexene and linear octene polycarbonates were found to have significant population of high molecular
weight molecules and hence they shear thin at a comparatively slower rate. The zero shear viscosity of cyclo hexene polycarbonate and terpolymer was highest amongst all aliphatic polycarbonates (although it was tested at maximum temperature). The high zero shear viscosity with apparent good melt strength and less die swell (as observed in melt flow indexer) makes cyclo hexene polycarbonate and the terpolymer as good candidates for blow molding applications.

5) Dynamic rheological spectra of the polymers show that the relaxation times for linear pentylene, linear hexene polycarbonate and linear octene polycarbonate are higher due to the presence of significant population of high molecular weight molecules. Cyclohexene polycarbonate and terpolymer also have large relaxation times due to stiff chains. Polyethylene carbonate and polypropylene carbonate have smallest relaxation times. From the combined dynamic rheological spectra of polycarbonates we observe that aliphatic polycarbonates can be divided into 3 groups rheologically. From the variation of $G'$, $G''$ and $\eta^*$ with frequency we see that linear pentene, linear hexene and linear octene polycarbonates form one group, polyethylene carbonate and polypropylene carbonate form the second group and terpolymer & cyclo hexene polycarbonate form the third group.
5.2. Future work:

Based on the correlations between the chemical structure of Aliphatic polycarbonates with their thermal, mechanical, relaxation and processing properties observed in this work, several suggestions can be made which may result in better understanding of aliphatic polycarbonates making them important materials of 21st century

1) The study of blending these materials and other techniques such as rubber toughening and study the effect of resulting structure on mechanical properties such as fracture toughness of polymer will give rise to new formulations and materials with desired mechanical performance. The effect of temperature and strain rate on the mechanical properties is also necessary to study.

2) The polymers have potential application as barriers and coatings. The study of the effect of structure on the vapor diffusion through the polymer will be important to study. The study of dielectric breakdown voltage is also important. Dielectric studies will also provide better understanding of the relaxation mechanisms in the polymers over wide range of temperatures and frequencies.

3) Rheometric studies over wide range of operating conditions of temperatures, pressures and shear rates will be necessary in practical scale up of processes using these polymers. The effect of blending and additives on the rheological properties will also be necessary for new product development.
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APPENDIX 1

CALCULATION OF ACTIVATION ENERGY FOR THE GLASS TRANSITION OF ALIPHATIC POLYCARBONATES

The plot of log (f) vs. $T_g$ is plotted for each polymer as shown below.

**Figure A1.1.** Plot of log(f) vs. $1/T_g$ for aliphatic polycarbonates obtained from DMA.
The Energy of Activation for the polymers can be calculated from the frequency
dependence of glass transition temperature in the graph above.

\[ \log(f) = A + \left( \frac{-\Delta E}{2303RT_{g}} \right) \]  
(A1 1)

Hence using the slope of the curve \( \log(f) \) vs \( 1/T_{g} \) we get.

Slope = \(-\Delta E/2303R\)  
(A1 2)

Where,

\[ R = \text{Universal Gas Constant} = 8314 \text{ J/mole K} \]

Hence \( \Delta E \) for each polymer is tabulated as shown below

**Table A1.1. Activation energies for aliphatic polycarbonates.**

<table>
<thead>
<tr>
<th>Polycarbonate</th>
<th>Slope of the curve</th>
<th>( \Delta E ) (J/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene carbonate</td>
<td>-19268</td>
<td>368927 1</td>
</tr>
<tr>
<td>Polypropylene carbonate</td>
<td>-13952</td>
<td>267140 9</td>
</tr>
<tr>
<td>Poly (linear pentene carbonate)</td>
<td>-12203</td>
<td>233652 6</td>
</tr>
<tr>
<td>Poly (linear hexene carbonate)</td>
<td>-15075</td>
<td>288643 2</td>
</tr>
<tr>
<td>Poly (linear octene carbonate)</td>
<td>-15149</td>
<td>290060 1</td>
</tr>
<tr>
<td>Poly (cyclo hexene carbonate)</td>
<td>-17571</td>
<td>336434 4</td>
</tr>
<tr>
<td>Terpolymer of CO2, propylene oxide (20%) and cyclohexene oxide (80%)</td>
<td>-19130</td>
<td>366284 8</td>
</tr>
</tbody>
</table>
APPENDIX 2.

CALCULATED AND OBSERVED GLASS TRANSITION TEMPERATURE FOR TERPOLYMER

The glass transition temperature of the terpolymer is calculated from the contribution of the two components and found to be in good agreement with the observed glass transition temperatures.

e.g. at 110 Hz $T_g$ for polypropylene carbonate = 330.35 K

$T_g$ for cyclohexene polycarbonate = 427.85 K

Hence, for the terpolymer synthesized using 20 wt % polypropylene oxide and 80 wt % cyclohexene oxide, the $T_g$ is calculated as

$$330.35 + 0.8(427.85 - 330.35) = 408.35 \text{ K}$$

The plot of the calculated and the observed $T_g$ of terpolymer for all the frequencies are tabulated as follows

Table A2.1. Glass Transition Temperature of Terpolymer

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>$T_g$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed</td>
</tr>
<tr>
<td>11</td>
<td>392.75</td>
</tr>
<tr>
<td>11</td>
<td>399.35</td>
</tr>
<tr>
<td>110</td>
<td>410.75</td>
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</table>
APPENDIX 3

STATISTICAL ANALYSIS OF STRAIN RATE DEPENDENCE OF MODULUS OF POLYETHYLENE CARBONATE

SAS program for the analysis of variance of the Modulus w.r.t Strain rate

data PEC,
  input name $ @ @ speed$ @ @,
  do i=1 to 5,
  input modulus @@,
  output,
  end,
lines,
  PEC1 20cm/min 4 83 6 12 5 13 5 48 4 21
  PEC2 50cm/min 8 06 5 88 6.18 5 60 6 02
  PEC3 100cm/min 7 92 7 58 10 24 9 16 7 31
  PEC4 10cm/min 3.00 3 08 3.10 3 90 3 09
;
proc anova,
  class speed,
  model modulus=speed,
run,
Output of the SAS program, which suggests that there is significant change in the modulus with the strain rate in polyethylene carbonate.

The SAS System
The ANOVA Procedure

Class Level Information

<table>
<thead>
<tr>
<th>Class</th>
<th>Levels</th>
<th>Values</th>
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<tbody>
<tr>
<td>Speed</td>
<td>4</td>
<td>100cm/min 10cm/min 20cm/min 50cm/min</td>
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</tbody>
</table>

Number of observations 20

The SAS System
The ANOVA Procedure

Dependent Variable: modulus

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<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Pr &gt; F</th>
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</thead>
<tbody>
<tr>
<td>Model</td>
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<td>71.41009500</td>
<td>23 80336500</td>
<td>30.50</td>
<td>&lt; 0001</td>
</tr>
<tr>
<td>Error</td>
<td>16</td>
<td>12 48740000</td>
<td>0 78046250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrected</td>
<td>Total 19</td>
<td>83 89749500</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

R-Square Coeff Var Root MSE modulus Mean
0.851159 15.24615 0.883438 5.794500

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Anova SS</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Pr &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed</td>
<td>3</td>
<td>71 41009500</td>
<td>23 80336500</td>
<td>30.50</td>
<td>&lt; 0001</td>
</tr>
</tbody>
</table>
VITA

Sudhir Dattatraya Thorat was born on October 7, 1976 in Aurangabad, in the state of Maharashtra, India. He received his Bachelor of Chemical Engineering degree from University of Mumbai (Bombay), Department of Chemical Technology (U D C T), in August 1998. He joined the Polymer Engineering program of Department of Materials Science and Engineering at University of Tennessee, Knoxville in December 1998 and received the degree of Master of Science in Polymer Engineering in December 2000.