ANALYZING AND IMPROVING VISCOELASTIC PROPERTIES OF HIGH DENSITY POLYETHYLENE

By

REAJ UDDIN AHMED

Bachelor of Science in Mechanical Engineering

Bangladesh University of Engineering and Technology
Dhaka, Bangladesh

2009

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
July, 2011

ANALYZING AND IMPROVING VISCOELASTIC PROPERTIES OF HIGH DENSITY POLYETHYLENE

Thesis Approved:

Dr. Jay C. Hanan

Thesis Adviser

Dr. Ranji Vaidyanathan

Dr. Sandip Harimkar

Dr. Mark E. Payton

Dean of the Graduate College

.

ACKNOWLEDGMENTS

First of all, I would like to show my heartiest gratitude to my supervisor, Dr. Jay C. Hanan, who has been very helpful throughout my entire Masters Program. His guidance, inspiration and support from the beginning of my graduate studies gave me constant motivation to perform this work. I consider myself lucky to be able to work under his supervision. I would also like to thank Dr. Ranji Vaidyanathan, for his immense help in this thesis. I worked in his lab for a major part of this work and his mentoring and constructive suggestions really mean a lot to me. I would also like to thank Dr. Sandip Harimkar for agreeing to be a member in my thesis committee.

I am also thankful to Niagra Bottling LLC, for funding the project. I would like to thank Dr. Tzuchia Erica Tseng and Mr. Bill Hall for helping me with the samples. I would also like to thank Dr. Liz Orwin for helping regarding equipments.

Special thanks go to Sudheer Bandla, who has always been very helpful and taught me many things. I would like to thank my colleagues Mazhar Islam, Ranjan Ganapthi Mahadevan, Massod Allakarami, Advait Bhat, Balaji Jayakumar, Rohit Vaidya, Praful Bari for their assistance in my work. My friends Krishnan Lakshminarayanan, Seshasai , Gandikota, Mrinalini Mulukutla, Sarat Das, Nazmul Khan Shahan, Mehedi Sarwar also helped me in many ways while I was working for this thesis.

Last, but not least, I would like to show my gratitude to my parents, brother and sister for their patience and understanding during my studies in abroad.

.

TABLE OF CONTENTS

LIST OF TABLES

Table Page

LIST OF FIGURES

Figure Page

CHAPTER I

1. INTRODUCTION

Polymers are widely used and relatively inexpensive material, comparable in importance to metals. Every year, new application areas are opening to utilize unique properties of polymers. New processing technologies are emerging to exploit the versatility of polymers and to take advantage of their ease of manufacture into all types of end products. Though the science of polymers has flourished relatively recently, people have been trying for years to improve the low quality of ancient polymers. Polymers are an integral part of everyone’s lifestyle with applications varying from commonplace domestic articles to sophisticated scientific and medical instruments. Today, more than 80% of world’s polymer market belongs to classes like Polyethylene (PE), Polypropylene (PP), Poly (vinyl chloride) (PVC), Polystyrene (PS) and Poly (ethylene Terephthalate (PET) [1].

1.1. Polyethylene (PE)

Polyethylene is a versatile engineering plastic compared to other polymers and alternative materials like glass, metal and paper. It is available in a variety of forms like polymer films, polymer containers, pipes, toys, and others. Polyethylene is a member of

The thermoplastic material group which means it can be melted or softened at elevated temperatures and can be molded or formed into new shapes repeatedly. Though PE is a chemically simple plastic material with the basic repeating unit ($-CH_2–CH_2-$), it is surprising that the first commercial scale production of this largest tonnage plastic started as recently as 1939 [1]. In addition to its low price, excellent processability, good electrical insulation properties over a wide range of frequencies, toughness, flexibility, very good chemical resistance, and in thin film of certain grades; transparency led PE to be one of the most promising plastic materials even after 70 years of its invention. Films of Polyethylene Terepthahalate (PET), PP, PA, and other plastic substrates are converted into water, gas, and aroma-tight films by extrusion coating with PE. As PE does not rust and is lighter than almost all metals, the varieties of PE resins are challenging traditional structural materials with reduced transportation and installation cost [2].

Polyethylene is a semicrystalline material whose crystalline lamellae contribute to the structural integrity while the amorphous part provides the more compliant elastic properties [3]. It is possible to obtain nearly one hundred percent crystallinity in polyethylene single crystal in dilute solution [4]. The semi-crystallinity of PE led it to be the most widely used mass produced plastic. The annual production capacity of PE was estimated at 79×10^6 metric tons in 2007 [5]. The relative molecular masses of all PE families are generally smaller than $M_r=3\times10^5$ [5]. The mechanical properties depend on the molecular weight and the degree of chain branching. PE has excellent chemical stability. It can be heat-sealed and has high barrier properties. Properties like stiffness, hardness, and strength increase with increasing density as higher density provides more crystallinity. However, increasing density also shows a decrease in some properties like impact resistance, toughness, resistance to stress cracking, cold resistance and transparency [5]. Details on the manufacturing process of ethylene as well as polymerization process of LDPE can be found elsewhere [6].

1.1.1. Types of PE

There are different types of PE having the same basic repeating unit with different properties and application. Molecular weight (MW), molecular weight distribution (MWD), density, percentage crystallinity, and degree of long chain and short chain branching are responsible for different properties in different types of polyethylene. Molecular weight and molecular weight distribution are the main factors that affect processability and mechanical properties of polyethylene. Due to the presence of shorter chains that act as a "lubricant," broad MWD material is easier to process. Short chain branching (SCB) can be introduced in PE through the use of comonomers (like 1-hexene). Interfering with the formation of lamellae, short chain branches contribute to the crystallinity and density of the semicrystalline polymer [7]. Classification of PE based on density is shown in Table 1 [8,9]. Low density polymer consists of branched molecules as opposed to high density polyethylene which is usually linear. Linear low density polyethylene (LLDPE) and HDPE possess spherulitic and lamellar morphology, while bundle-like crystals embedded in amorphous material can be seen in plastomers and elastomers.

Table 1: Different types of Polyethylene

PE Type	Density(g/cm^3)
Very Low Denstiy Polyethylene (VLDPE)	<0.910
Low Density Polyethylene (LDPE)	0.910-0.925
Linear Low Density Polyethylene (LLDPE)	0.915-0.925
Medium Density Polyethylene (MDPE)	0.926-0.940
High Density Polyethylene (HDPE)	0.945-0.965
Ultra High Molecular Weight Polyethylene	>0.965

1.2. High Density Polyethylene (HDPE)

HDPE is a Polyethylene thermoplastic made from petroleum and represents the largest portion of PE produced. HDPE is more rigid and harder than LDPE. LDPE can have crystallinity around 40% whereas HDPE has crystallinity of around 90% [6]. Due to its higher crystallinity, HDPE is much stiffer and stronger than LDPE. HDPE possess good compressive strength and its tensile strength is four times higher than LDPE [10]. Mechanical properties like shrinkage, wear resistance, modulus, and hardness depend on crystallinity and are found higher in HDPE than LDPE. Permeability by gases is also significantly lower for HDPE than LDPE. It has permeability of about one-fifth that of LDPE [7]. As HDPE is less branched, it is more stable in oxidation than LDPE. Creep is generally less pronounced in samples with high crystallinity. Moreover, higher density also provides good creep resistance. As HDPE possess both higher crystallinity and density than LDPE, better creep resistance is noticeable in samples made with HDPE [11].

HDPE is universally recognized as a 'safer' plastic when it comes to water storage. HDPE meets the U. S. Food and Drug Administration (FDA) requirements for direct food contact applications. It also fulfills requirements of the US Department of Agriculture (USDA), National Sanitation Foundation (NSF), and the Canadian Department of Agriculture regarding food contact applications. HDPE provides good processability for injection molding, blow molding and extruded items, which makes it a preferred material in manufacturing products like personal care, household industrial containers and bottles. As moisture and water have no affect on HDPE, it can be used in freshwater and saltwater applications [10].

Worldwide application of HDPE is increasing with rapidly growing industries, especially those of packing and construction. The global market of HDPE reached 36×10^6 tons in 2007 [5] from 22×10^6 tons in 2000 [12]. North America and Western Europe was responsible for 44% of global demand in 2007. Whether it is bottle caps, carrying bags, or buckets; HDPE shows its unparallel properties to be an integral part of everyday life. Almost one third of toys are made from this thermoplastic. Other vital products like water pipes, oil tanks, or geomembranes are large application areas of HDPE. Being non-toxic and light weight, HDPE is increasingly used as an alternative to less environmentally friendly substances. Milk bottles and other hollow goods manufactured through blow molding are an important application area of HDPE and almost one third of the world production is applied here [12]. The wide application range of HDPE includes arena board (puck board), telecom ducts, laundry detergent bottles, milk jugs, fuel tanks for vehicles, watering cans, plastic lumber, folding chairs, folding tables, plastic bags, natural gas distribution pipes, water pipe, bottles, and others. Films made out of HDPE posses high fat resistance (as wrappers for meat) and have better aroma barrier properties compared to lower density PE materials [5].

During its early age of production, PE was manufactured using a high pressure polymerization process of ethylene, which led to a relatively low molecular weight polymer. Development of Ziegler catalysts in 1953 allowed a relatively higher density of polyethylene, which was named High Density Polyethylene (HDPE). The Philip and standard oil process, developed in the 1950s, also used to produces HDPE with a density of 0.96 gm-cm^{-3}. HDPE can be produced mainly by two methods. The first method involves coordination of polymerization of the monomer by triethyl aluminum and titanium tetrachloride. The second method uses metal oxide catalyst for polymerization. Chromium or molybdenum oxides, supported over alumina-silica bases can be used as metal oxide catalysts. In both methods, the polymerization is carried out at relatively low pressure [6].

1.3. Viscoelasticity, Creep, and Stress Relaxation of Polymers

Viscoelasticity is the property of a material having both viscous and elastic characteristics in deformations. Polymers are viscoelastic materials and they do not conform to simple models of material behavior. Figure 1 shows a typical viscoelastic response of polymers. Here, an instantaneous elastic response (strain ε_e) quickly gives rise to a strain-time curve, with slope decreasing with time [13]. However, the strain continues to increase throughout the entire application period of the load. Strain in polymers is composed of both a delayed elastic strain and a viscous flow component.

Instantaneous strain in polymers is due to bond stretching and bending, and the delayed elastic response is due to a process like chain uncoiling. Viscous flow is attributed to the slipping of chains past each other. Most solid polymers show a limiting value of strain (ε_u), and the slope of the constitutive curve approaches zero. Unloading of polymers is followed by immediate recovery of the instantaneous elastic strain and slower recovery of the delayed strain. The viscous flow component will remain [13].

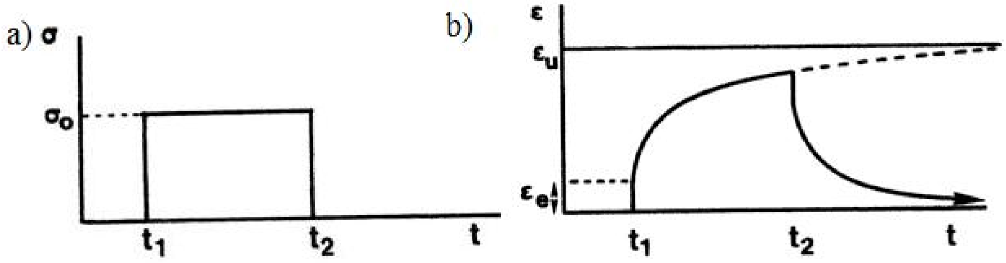

Figure 1: a) Stress applied for time t_1 and t_2 b) Response of a viscoelastic material [13]

The viscoelastic nature of polymers is usually described by a compliance, *C(t, T)*, which is a function of both time and temperature. Figure 2 depicts the stress strain curves for elastic, linear viscoelastic, and non-linear viscoelastic materials at a fixed temperature. Unlike viscoelastic materials, elastic materials do not show dependency on the application period of loads. Linear stress strain curves can be generated from linear viscoelastic materials, if the measurements of strain are made precisely at the same time after application of the load in each case. Measurements at a greater time will produce larger strains for the same load. On the other hand, nonlinear viscoelastic materials do not produce linear stress strain curves for fixed loading time. Different models are available to describe linear viscoelastic behavior while nonlinear viscoelasticity is not that easy to treat and only recently some theories have emerged. Generally polymers are linear viscoelastic materials at lower strains and shorter times (up to 0.3% strain and 100 seconds) and nonlinear at higher strains [13].

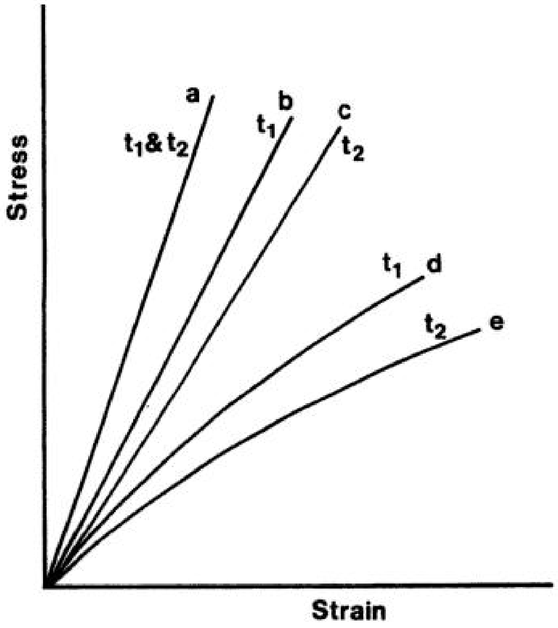

Figure 2: Stress strain behavior of a) an elastic solid loaded for times t_1 and t_2; b) and c) a linear viscoelastic solid loaded for times t_1 and t_2; d) and e) a non linear viscoelastic solid loaded for times t_1 and t_2.In all cases $t_2 > t_1$ [13]

Creep is one of the basic behaviors directly related to performance. It is fundamental to understanding polymeric relaxation. Creep can be described as the tendency of a material to slowly deform as the material is exposed to a constant load over time. Polymeric creep is different than metallic creep, as the latter involves permanent deformation while polymer creep is recoverable on removal of the load [13]. Colak *et al.*

[14] stated that the delayed response of polymer chains during deformations is responsible for the creep behavior of polymers. When initially folded chains reach a new equilibrium configuration, deformation stops. In the same reference, it is stated that the creep response of polymers is dependent on the microstructure of the polymers. Crystalline polymers show very little creep strain above the glass transition temperature compared to the same material in the amorphous rubbery state. Heavily cross-linked polymers, such as epoxy, showed good creep properties at room temperature compared to less cross-linked polymers, like polyethylene. Stress relaxation is also a consequence of delayed molecular motion. Creep-recovery testing is also used as a powerful tool to analyze a material's properties, which allows understanding of a material's response to constant load and its behavior upon removal of that load. Creep tests involve a sample with set load and observation of the strain change over time. Recovery tests involve observation of the relaxation of a material once the load is removed. Stress relaxation is opposite creep behavior. It describes how polymers relieve stresses under constant strain [15]. Polymers are viscoelastic materials and they behave in a nonlinear and non-Hookean fashion [16]. This nonlinearity of polymers can be described by both stress relaxation and creep.

1.3.1. Simple Model for Creep and Stress Relaxation

General creep and stress relaxation behavior of polymers can be explained by a very simple model, but only the time scales are collapsed in the models compared to actual materials [17]. In models, substantial changes are observed in about one decade of time while polymers show the same amount of changes only over many decades of time.

The Maxwell unit is used as a simple model for stress relaxation where a Hookean spring and a Newtonian dashpot are connected in series as shown in the insert in Figure 3. In a stress relaxation experiment, the model is given a definite strain *ε* and the stress *σ* is measured as a function of time. If the modulus or stiffness of the spring is *E*, and the viscosity of the dashpot is *η*, we can formulate the change in elongation of the spring, which is compensated by an equal change in the dashpot in strained model as

$$\frac{d\varepsilon}{dt}=\frac{1}{E}\frac{d\sigma}{dt}+\frac{\sigma}{\eta}=0-------------(1)$$

As for spring $\varepsilon=\frac{\sigma}{E}$ and for dashpot $\frac{\sigma}{\eta}=\frac{d\varepsilon}{dt}$, the solution of this equation of motion is

$$\frac{\sigma}{\sigma_o}=e^{-Et/\eta}=e^{-t/\tau}---------------(2)$$

Where, $\tau=\frac{\eta}{E}$ is relaxation time.

According to this model, all initial deformations are carried out by the spring while at a later time, the dashpot starts to relax allowing the spring to contract. Equation 2 is plotted in two different time scales and shown in Figure 3 and Figure 4 for typical values of an elastomer. The stress relaxation curve of Figure 4 has a maximum slope and a stress ratio of σ/σ_o= 0.3679 or e^{-1} at the time τ. Stress relaxation can also be expressed in terms of Stress relaxation modulus $E_r(t)$.

$$E_r\,(t)=\sigma/\varepsilon=\frac{\sigma_o}{\varepsilon}e^{-t/\tau}---------(3)$$

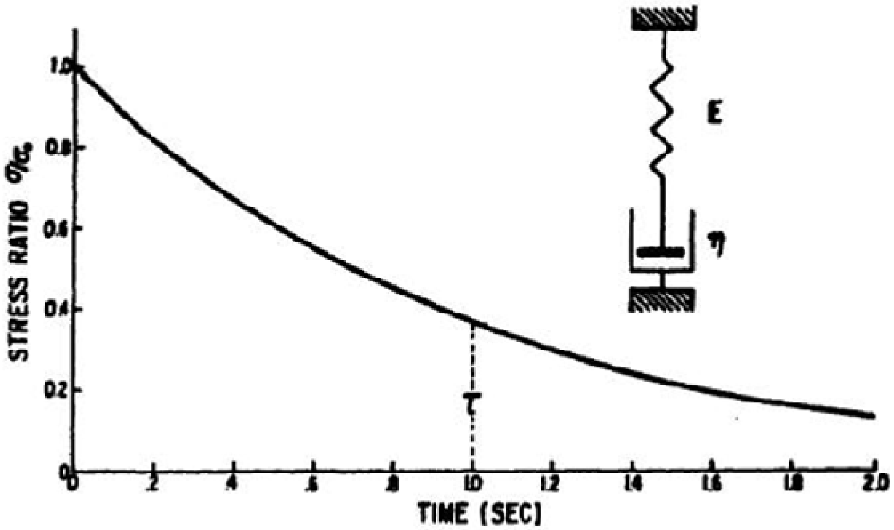

Figure 3: Stress relaxation of a Maxwell model (linear scales) τ =1 s [17].

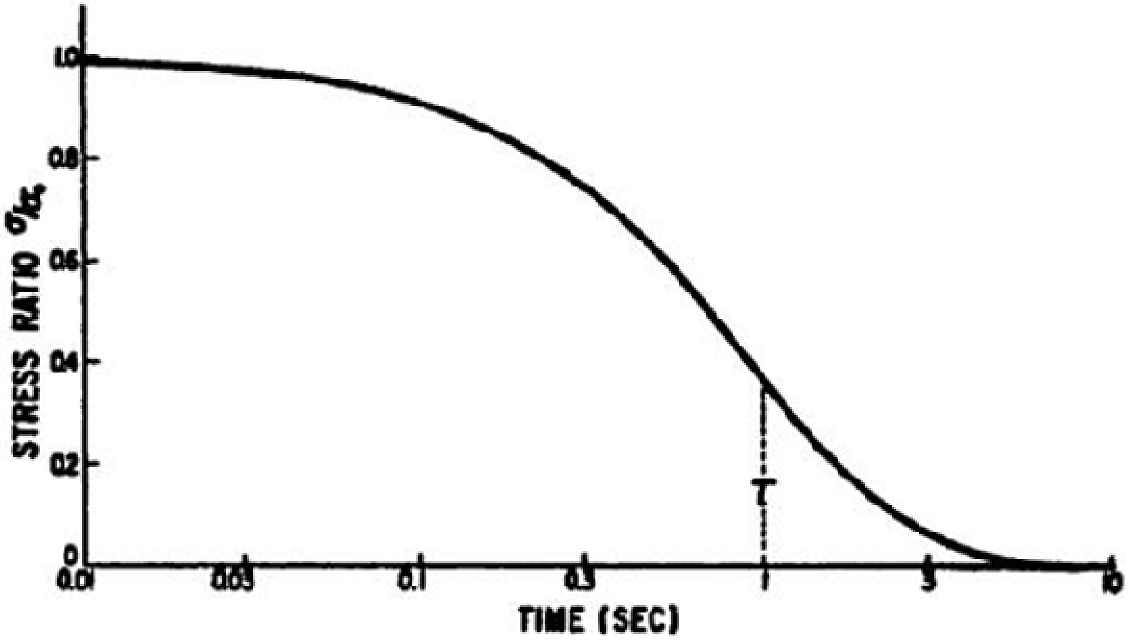

Figure 4: Stress relaxation of a Maxwell model on a logarithmic time scale. Model same as Figure 3 [17].

Creep behavior can be described by the four-element model shown in Figure 5. As soon as constant load is applied, a single spring with modulus E_1 gives the initial elongation. Later, elongation is contributed from the spring E_2, and dashpot η_2 in parallel, and from the dashpot with the viscosity η_3

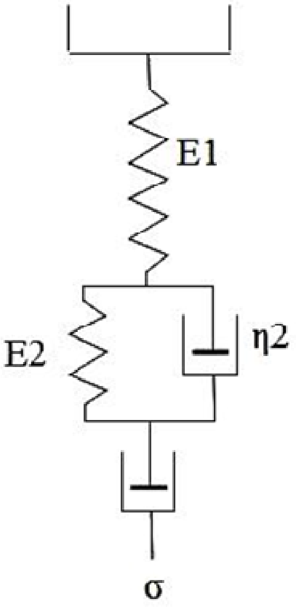

Figure 5: Four-element model of Creep [17].

Total elongation is the summation of individual elongation of the three individual parts. Therefore, we can write,

$$\varepsilon = \frac{\sigma_o}{E_1} + \frac{\sigma_o}{E_2}(1 - e^{-t/\tau}) + \frac{\sigma_o}{\eta_3} t \text{ --------------(4)}$$

Here applied stress is σ_o and $\tau = \eta_2/E_2$ is the retardation time. During the recovery test, when the load is removed at time $t_{1,}$ the creep is recoverable except for the viscous part due to dashpot η_3. Instant reduction in the elongation of the model ($=\frac{\sigma_o}{E_1}$) can be found as soon as the load is removed. A Creep recovery equation can be shown as,

$$\varepsilon = \varepsilon_2 e^{-(t-t_1)/\tau} + \frac{\sigma_o t_1}{\eta_3} \text{----------------------------------} (5)$$

Where $\varepsilon_2 = \frac{\sigma_o}{E_2}(1 - e^{-t_1/\tau})$

Creep and recovery of a four-element model is illustrated in Figure 6, and in Figure 7, for some particular constant [17]. In the model, most of the recoverable creep occurs within about one decade of the retardation time [17]. Figure 7 depicts how the curve is changed along with different constants in the model.

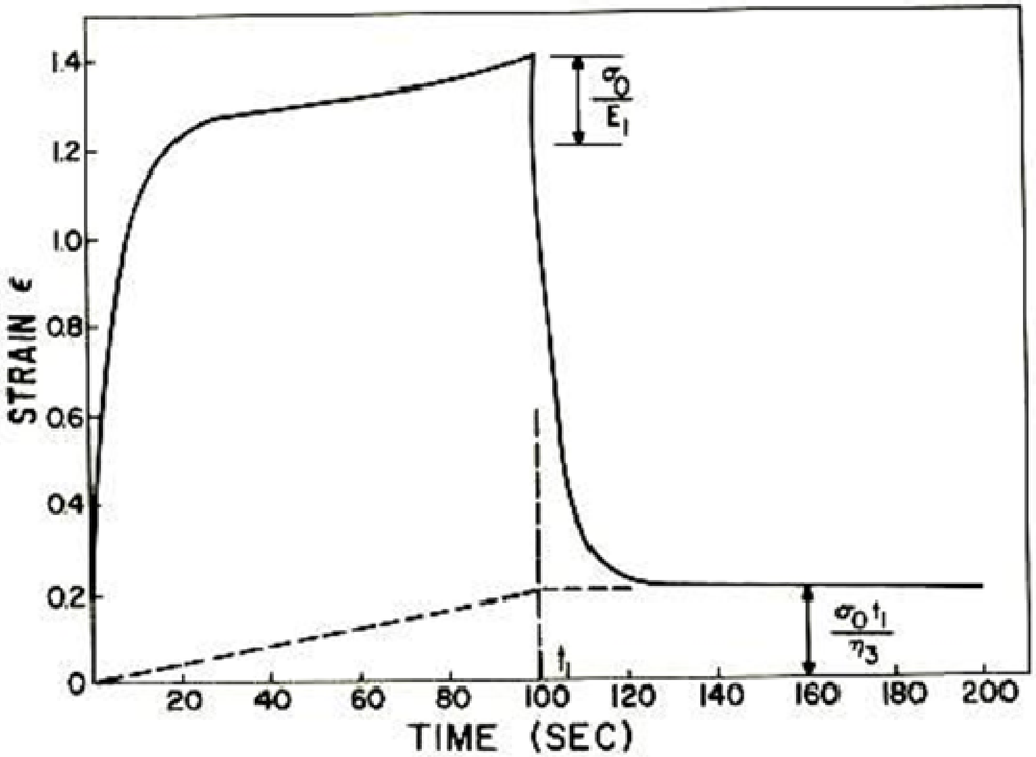

Figure 6: Creep strain and recovery strain of a four-element model

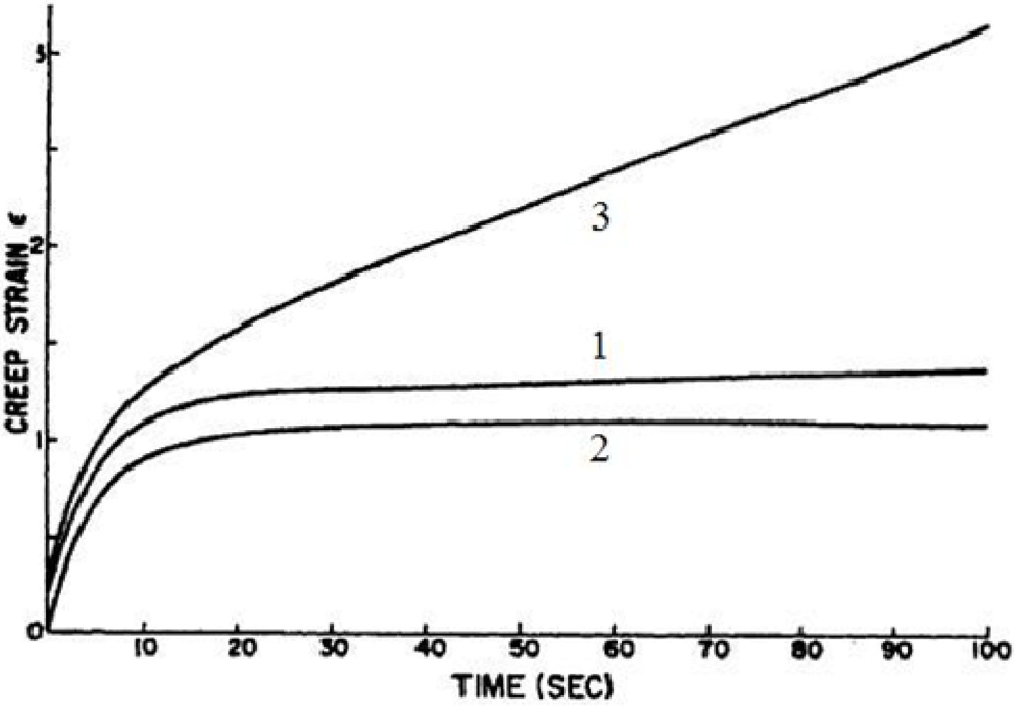

Figure 7: Creep of a four-element model: Curve 1 is the same as Figure 6, curve 2 shows only a small amount of viscous creep, curve 3 shows creep with prominent viscous flow [17].

CHAPTER II

2. OPTIMIZATION OF HDPE PROPERTIES

2.1. Motivation

Due to its low cost, excellent properties, and recyclability; HDPE is being used as plastic containers and bottles for containing consumer products, as well as industrial chemicals like, alcohols and acid for long times. HDPE is more often used in the container of liquids that are stored at atmospheric pressure [18,19,20]. After production, these containers are stored in plant or distribution center warehouses for extended periods. Stacked containers experience static loading and deformation strain during their entire storage time, so dimensional stability, and time dependent properties become significant. For these reasons, particular attention should be devoted to study the stacking phenomena, to determine the time limit that HDPE containers can be stacked without damage, and to determine the maximum tolerable deformation. Considering a polymer's behavior and its response to long term loading, maximum storage time can be predicted from theoretical models [21,22]. Therefore, proper understanding of the viscoelastic properties of HDPE, with relevant FE simulation, can facilitate improved designing, and can solve different practical problems associated with long term storage of the final products in warehouses. Because of the time-dependent behavior of polymers, researchers focus on its viscoelastic behavior through experiments like creep and stress relaxation. Provoked by all these reasons, mainly viscoelastic properties, creep behavior and stress relaxation of HDPE were investigated as part of this thesis. Now, light weighting is a driving force in plastic industries, which results in material removal from existing designs. As a result, time dependent properties like viscoelasticity also need to be understood and improved along with other engineering properties like, strength, toughness, and load bearing capabilities. Motivated by this, we investigated several approaches described in section 2.3, to improve existing viscoelastic properties in neat and untreated HDPE. HDPE used in the packaging industry requires several important properties such as, strength, chemical inertness, food grade approval, low permeability, and aesthetic appeal. Several approaches to improve viscoelastic properties of HDPE carried out in this thesis were carefully chosen, so that they do not have a negative impact on the abovementioned properties.

2.2. Viscoelasticity of HDPE

Extensive works regarding the viscoelasticity of HDPE can be found in literature. It is usually assumed that a tensile creep test is a good measure of viscoelasticity [23]. However, viscoelastic behavior of HDPE under compressive loading has also been studied. Elleuch [24] *et al.* studied the viscoelastic behavior of HDPE under tensile and compressive loading and showed the influence of strain rates on monotonic tensile and compressive tests. They showed the mechanical response of HDPE is nonlinear at a wide range of strain rates and depends on the strain rate. Elleuch *et al.* investigated long term creep and stress relaxation of HDPE and concluded that for both compression and tensile tests, the viscoelastic behavior of the HDPE at low stress or strain level is linear within monotonic domains. They showed that associated normalized curves for different stress or strain could be represented by a single curve, characterizing the compressive creep compliance or stress relaxation versus time. Nakayasu *et al.* [25]presented the viscoelastic behavior of HDPE over a wide time scale and a considerable span of temperature and measured creep and dynamic mechanical properties in torsion. Several models can be found in literature to predict the creep and relaxation tests of polymers. Findley [26] describes a theoretical model where the total deformation is used as the sum of elastic (ε_o) and inelastic (ε_c) elements, which depends on temperature, time and loading intensity. Elleuch *et al*. used Findley's model to predict the tensile creep curves of HDPE, but the experimental value did not match with the value found by the model. Zhang *et al.* [27] developed nonlinear viscoelastic (NVE) and viscoplastic (VP) constitutive models using their experimental data, and found the models to predict the properties with some constrains. Elleuch *et al*. [28] also proposed a mathematical model based on the gradient method and found the experimental compressive creep or relaxation results at low stresses and strains are in good agreement with the values predicted by the model. Elleuch predicted the maximum storage time of filled tanks to avoid the critical value of deformation of filled tanks. Colak *et al*. [29] modeled the viscoelastic and viscoplastic behaviors of HDPE under uniaxial monotonic and cyclic loading. Processing conditions also influence the viscoelastic behavior of HDPE. Mano *et al*.[30] compared the viscoelastic properties of HDPE samples processed at a conventional injection molding machine with the samples processed at Shear controlled orientation in injection molding (SCORIM). They found higher creep strain for the HDPE made by conventional injection molding. Mano *et al* observed the wide spread of relaxation time for both types of samples, which is ascribed to the molecular mobility of the amorphous phase involved in the relaxation process.

2.3. Approaches

The quest for high mechanical and viscoelastic properties in polymeric materials has resulted in several approaches. Synthesis of new materials or modification of existing materials, with chemical (e.g. grafting, branching or cross-linking) or physical treatment (e.g. blending, compounding or annealing) facilitates enhanced properties in polymers [30]. Making composites using additives is one of the most accepted methods for improving properties of polymers.

2.3.1. Additives: $CaCO_3$

Many industries have been trying for years to find cost effective filler additives for strengthening HDPE properties. But the main concern of the filler searching process is, the filler should not affect melt processability of the resin and should not be detrimental to the quality or overall mechanical performance of the product [31,32,33]. Inexpensive inorganic substances, such as calcium carbonate ($CaCO_3$), mica, wollastonite, glass fiber, glass beads, jute and silica (SiO_2) are widely used in plastic industries to improve the mechanical and thermal properties [34,35,36]. Micro- and nano-fillers have been attracting researchers in recent days, because they exhibit remarkable improvement in material properties compared to conventional composites made by macro-fillers [37]. Compared to macro-fillers these micro-or nano-composites need lower loading of fillers. Different kinds of filler materials have been used in literature to reinforce HDPE [38,39,40]. Different kinds of mineral particles can be used in HDPE to improve dimensional stability, opacity and barrier properties. Because of its low cost and abundance, $CaCO_3$ is the largest volume mineral used in the polymer industry. More than 80% of the fillers used in thermoplastics are based on $CaCO_3$ [41]. The effect of $CaCO_3$ on the properties and performance of polymers with different particle size, concentration, surface treatment, and microstructure has been studied and reported in different scientific papers [42,43,44,45]. Motivated by all these reasons, $CaCO_3$ was incorporated in HDPE to improve its time dependent properties.

Nielson *et al.* [46]suggested that particulate fillers affect the relaxation and retardation time distribution, and showed a relationship between creep strain of the filled system at a given time to the corresponding strain of the unfilled polymer in the following way,

$$\frac{\varepsilon_c(t)}{\varepsilon_1(t)} = \frac{E_1}{E_c} -------------(6)$$

Here E is the elastic modulus, ε is the strain, and t is the elapsed time. The subscript *1* denotes the unfilled polymer, while *c* denotes the composite. Equation (6) is used to describe the creep behavior of kaoling filled polyethylene [46, 47] and is valid only if no dewetting at the filler surface occurs. Creep strain will exceed the prediction of Equation (6) if dewetting takes place. Dewetting is often noticed at high strain levels, long times, and high filler concentrations. There is evidence that chemical and physical interaction between the polymer and the filler can significantly affect the properties of composites [48,49,50,51]. Surface treatment of filler materials can pronounce these interactions and can create an interphase region close to the filler surface with properties different from that of the remaining polymeric matrix. Such inter phase regions can cause deviation of the properties of the composite from predictions (6).

For unfilled polymers, the relation between the maximum slope of the relaxation curve and the initial stress σ_0 of the relaxation experiment can be expressed as [52,53]

$$F = \left(-\frac{d\sigma}{dl \ln t} \right)_{\max} = (0.1 \pm 0.01)(\sigma - \sigma_i) -------------- (7)$$

Where σ is the stress. Ek, *et al* [54] studied the effect of fillers on the internal stress level (σ_i) of polyethylene and showed that, despite the variation of σ_i caused by fillers, Equation (7) is valid for filled polymers too. They compared the stress strain curve of $CaCO_3$ filled HDPE with unfilled HDPE, and compared experimental results of the tensile modulus vs. $CaCO_3$ content with the value found from Lewis Nielsen Equation [46,55]. They assumed $CaCO_3$ as spherical to apply the Lewis Nielsen's equation and found the predicted data in good agreement with the experimental data. They found an 83% increase in the modulus by adding 50 wt% $CaCO_3$ to HDPE. For stress relaxation tests, they found higher relaxation values of stress for 50 wt% $CaCO_3$ filled HDPE over the unfilled HDPE at longer times. They evaluated internal stress by a method suggested by Li [56], and also found that the power law ($\dot{\sigma} = -B(\sigma - \sigma_i)^n$) is suitable for both filled and unfilled HDPE. They found the internal stress level, calculated from relaxation data markedly increased with the filler content. Ek *et al.* stated that the presence of filler particle might have induced a structure change of the polymeric matrix close to the filler surface, which restricts the macroscopic flow. They mentioned an increase in internal stress with increasing filler content also justifies such conclusion. The increase in internal stress provides more restriction on the flow as a result, low creep strain is observed with increasing filler content. They used dynamic mechanical analysis to explain change in structure of the surrounding area of $CaCO_3$ in HDPE, similar to the process described by Kosfel *et al.* [*57*]. From the loss modulus vs. temperature graph, they found obvious peak for the □-transition. Incorporation of $CaCO_3$ shifts the □-peak to somewhat lower temperatures [54]. They observed noticeable β-transition after immersion the composites in CCl_4 for 1 hour. They observed, addition of $CaCO_3$, broadened the β-transition, and shifted it to somewhat higher temperatures. They explained, reduction of the mobility of the polymer molecules absorbed on the filler surface was responsible for the broadening and shifting of the β-transition. Therefore they concluded, structure of the polymers changed to some extent with $CaCO_3$ and an interphase region close to the filler surface was created. Different methods for measuring internal stresses of polyethylene can be found in another paper of Kubat *et al*. [58]. Some other researchers also investigated the viscoelasticity, creep and stress relaxation in HDPE-$CaCO_3$ composites. Yang *et al.* [59] investigated the relaxation and crystallization of HDPE reinforced with $CaCO_3$ particles. They observed the addition of $CaCO_3$ significantly increases the storage modulus but it has very little effect on tan delta. They also observed treatment of $CaCO_3$ filler particles have very little effect on the mechanical, viscoelastic, and morphological properties of the composites. Elleithy *et al.* [60] investigated the viscoelastic properties of injection molded HDPE-$CaCO_3$ composites and neat HDPE, via torsional and rotational techniques. At low frequency, they observed higher shear modulus of the HDPE-$CaCO_3$ composites than the shear modulus of neat resin. However, at higher frequency they observed less difference in shear modulus between the neat resin and HDPE-$CaCO_3$ composites. They also observed higher complex viscosity for the HDPE-$CaCO_3$ composites than the neat HDPE. Grabowska *et al*. [61] also found significant increase in viscosity at lower shear rates for the $CaCO_3$ filled HDPE. The creep behavior of HDPE-$CaCO_3$ composite is dependent on the amount of $CaCO_3$content. Sahebian *et al.* [62] suggested that the best creep behavior of PE nanocomposites can be achieved with 10% of $CaCO_3$ incorporated in it. Besides viscoelastic properties, incorporation of $CaCO_3$ also improves the mechanical properties of HDPE resins. Grabowska *et al*. [61] showed that incorporation of $CaCO_3$ improves modulus and impact strength of HDPE without detrimental effects on the elongation and break strength. The increase of modulus with $CaCO_3$ also confirmed by Lazzeria *et al* [63] and Yang *et al*. [59]. Dai *et al*.[64] reported that mechanical properties were reduced for untreated $CaCO_3$ in HDPE, but treated $CaCO_3$ enhanced mechanical properties. Grabowska [61] found that incorporation of $CaCO_3$ also facilitates the processing of recycled HDPE, by preventing segregation of polyolefin with different MFIs, and by improving melt homogeneity, mechanical properties, and extrusion output. They showed that the extrusion processability of the filled HDPE resin blends would be similar to the unfilled resins.

Crystallinity is an important parameter for the properties. The dispersed nano-scale filler can enhance the crystallization rate of the PE matrix by acting as a heterogeneous nucleation agent, while, at the same time, it can hinder the transport of the molecule chains to reduce the crystallization growth rate [65]. Grabowska *et al*. [61]

found that incorporation of $CaCO_3$ in HDPE lowers the crystallinity. However Ek *et al*. [54] and Elleithy *et al*.[60] found very little effect of $CaCO_3$ in crystallinity and melting point of HDPE. They found some agglomeration of $CaCO_3$, and suggested that due to its higher polar nature and higher surface areas; $CaCO_3$ is not easy to well disperse and stabilize in the polymer matrix. $CaCO_3$ has a great tendency to agglomerate. The agglomeration of $CaCO_3$ increases with decreasing of the particle size [66]. Mechanical interlocking, electrostatic forces, and van der waals forces could be the principle adhesive forces between the particles [67,68]. Poor dispersion and adhesion of filler often results in poor physical properties in the final products. Sometimes poor adhesion quality of $CaCO_3$ can be of beneficial effect on polymer matrix by enhancing breathability of polymeric films [60]. However, Ek *et al.* [54] did not find any dewetting or lack of adhesion between the HDPE matrix and $CaCO_3$ filler. They observed well dispersed $CaCO_3$ in HDPE, without any tendency of filler agglomeration.

2.3.2 Ageing and Annealing

"Ageing" may be defined as the change of the properties of polymers over a period of time. This change may be of engineering properties, like strength and toughness, or of physical characteristics, like density or of chemical characteristics, like reactivity towards aggressive chemicals [69].

Physical ageing is the most common form of ageing in polymers. When polymers are in a non-equilibrium state, molecular relaxation drives the material closer to equilibrium, and as a result, physical ageing occurs. Non-equilibrium sates are encountered during the shaping of thermoplastics through extrusion, injection molding, or blow molding when the polymer is cooled rapidly from an elevated temperature.

2.3.2.1. Ageing in Amorphous Material

If amorphous polymers are cooled below the glass transition temperature, the rate of molecular relaxation is too slow to keep pace with the changes required, if the materials are to remain at thermo-dynamic equilibrium. So when the materials reach thermal equilibrium with the surroundings, they are not at thermodynamic equilibrium. This instability provides a driving force so a material's properties may change over an extended ageing period. Iacopi and White [70] showed the effect of ageing on injection molded polystyrene bar and found higher density of the bar with more ageing time. The change of density depends on the ageing temperature (T_a). If T_a is not far below the glass transition temperature (T_g), the ageing may be quite rapid, but still ageing effects can be found after many years. If T_a is far below the T_g, the kinetics slow with increasing difference between T_g and T_a, and this will limit the rate of change. Struik [71] studied the physical ageing of amorphous materials and examined creep behavior of materials in different states of ageing. Struik's data and analysis were in good agreement with the engineering properties, and showed close connection with some other author's works; including Kovacs, Hutchinson, McCrum, McKenna and others [72,73,74,75,76,77,78].

2.3.2.2. Ageing in Semi-Crystalline Materials

Most research regarding ageing of polymers has been concentrated on amorphous polymers. Ageing in semi-crystalline polymers is more complex than ageing in amorphous polymers. In semi-crystalline polymers, even though the crystalline phase is relatively inert with respect to ageing, it influences the relaxation process of the surrounding amorphous phase. The crystalline phase restricts the relaxation process in the adjacent amorphous phase, which mainly depends on the morphology, and on the interaction between the crystal, and amorphous region. So even though the change of properties due to ageing mainly depends on the amorphous phase, it is controlled partly by the presence of the crystalline phase. Moreover, crystallinity, which has the main impact on mechanical properties, may also get changed by ageing. That is why the effect of ageing is as pronounced in semicrystalline polymers as amorphous polymers. Besides the contribution of amorphous phase of the semi-crystalline polymers, secondary crystallinity [79,80], and molecular rearrangement can be potential source of ageing.

During the processing of polymers, the rate of crystallization is maximum at some temperature $T_{c,max}$, which is between the mold temperature and the melt temperature (T_m). Even at T_m, the rate of crystallization is often quite slow and the rate is also slow at ambient temperature after demolding. Therefore, crystallinity is often incompletely developed immediately after injection molding, extrusion, or blow molding processes. The molecular mobility often allows molecular segments in the amorphous phase to realign, and to crystallize. This realignment and crystallization could be either in the form of new crystals between the pre-existing lamellar crystals, or by adding to the pre-existing crystals. In highly crystalline polymers, such as polyethylene, the mobility is particularly high, where the glass transition temperature T_g is far below the ambient temperature. In those cases, secondary crystallinity occurs quite fast. Secondary crystallization causes local shrinkage in materials and hence develops residual stresses in solid polymers. This has been observed and analyzed by White [80], Siegmann and Kenig [79]. Very small change in crystallinity (of the order of 1%) can result in large property changes in polymers. McCrum [81] considered the effect of crystallinity in his investigation, but Struik [82] claimed that secondary crystallization is not strong enough to explain his ageing observation with polypropylene. In some of his other papers [83,84,85,86] Struik concentrated on the behavior of the amorphous phase to interpret his data about the physical ageing of semi-crystalline polymers. He explained the effect of the presence of the crystal unit in the amorphous phase on molecular relaxation [84].

2.3.2.3. Residual Stresses and Ageing

The rapid cooling during the processing of thermoplastics often causes the formation of strong temperature gradients, and as a result, residual stresses develop [87]. These residual stresses have significant effects on the properties of polymers and may relax partially or completely over extended ageing. For amorphous polymers, the relaxation of residual stresses depend on the glass transition temperature, while, for semi-crystalline polymers, it depends on the crystallinity. Generally the residual stresses relax relatively fast at short ageing times, and the rate slows down progressively. The final residual stress level, after extended periods of time are often a significant fraction of the initial residual stresses values. This phenomenon can be better understood in terms of the stress-biased relaxation behavior [88,89,90,91]. The “site-model theory” [3] predicts that stress relaxation in a polymeric body does not reduce the stress to zero [88], and so residual stresses are therefore expected to equilibrate at some non-zero level [91]. The site-model theory predicts behavior that is similar to that of a standard linear solid [89]. Elevated temperature changes both the equilibrium state and the rate at which equilibrium is reached. Several examples of change in residual stress distribution during ageing at elevated temperature can be found in Refs. [92,93,94].

2.3.2.4. Annealing

Annealing of polyethylene involves reheating of the polymers for a definite period of time after they have been processed. Polymeric molecules are kept in stressed position during the manufacturing process such as injection molding or extrusion. A sudden drop of temperature during the demolding process freezes the molecules at whatever positions they were inside the mold. Annealing removes these frozen or residual stresses and allows them to go back to their natural random state. Crystallinity is also related to annealing. Crystals can grow over time until equilibrium at the annealing temperature. Relaxation of the residual or frozen stresses can improve tensile strength, impact strength, and slow crack growth characteristics [95]. While rapid cooling suppresses the formation of crystals and gives tough, clear products, annealing or slow cooling provides relatively brittle and hazy products [96]. Annealing at high pressure also leads to the formation of large crystallites with relaxation of stressed chains, and hence increases molecular mobility in amorphous regions [97].

Tiemprateeba *et al*. [98] studied the effect of annealing on neat and $CaCO_3$ filled HDPE, and reported that melting temperature, crystallinity, modulus, and tensile strength increase with increasing annealing temperature. They annealed the samples at different temperatures for 1 hour and then furnace cooled them. For unfilled polymers, both the degree of crystallinity, and melting temperature increased with the increase of annealing temperature. The improvement of these properties stabilized at an annealed temperature of 135-140^{o}C, and further increases in temperature did not significantly alter the thermal properties. The modulus and yield stress of the samples increased, at annealing temperature (T_a) greater than 120^{o}C. Both the modulus, and yield stress increased with the increasing of annealing temperature, and after 135-140^{o}C, no significant improvement was observed. Yield strain did not show any relevance with annealing temperature. For the filled composites, the degree of crystallinity, and melting temperature did not depend on the percentage of filler materials, but depended on annealing temperatures (increased as T_a increases). Modulus was found to increase with increasing of filler contents. However, yield strains and tensile strengths were observed to decrease with increasing filler contents. Annealing showed much higher modulus and tensile strength for the filled composites.

Annealing can improve modulus more than radiation effects. Suwanprateeb *et al.* [99] examined annealing at 37^{o}C. They showed that thermal ageing (annealing) can improve modulus for both neat HDPE and hydroxyapatite (HA)-HDPE composites, while gamma radiation at 25^{o} kGy did not show such significant improvements in modulus values. They observed around 4% increases in crystallinity due to annealing of the samples. They reported creep resistance can also be increased by annealing.

CHAPTER III

3. MATERIALS AND METHOD

3.1. Dynamic Mechanical Analysis (DMA)

3.1.1. Introduction and Working Principle

Dynamic Mechanical Analysis (DMA) is becoming a more common tool in the analytical laboratory. DMA is a material characterization technique where the sample is mechanically deformed in a cyclic manner, and the response is measured instantaneously. The deformation and response is used to study material behavior under stress, temperature, frequency, and other values.

Figure 8 shows the working principle of DMA. It shows the sinusoidal stress created by oscillatory forces of DMA, which generates corresponding sinusoidal strains. For purely elastic materials, the deformation will start as soon as the force is applied. For purely viscous materials, there should be a 90^o phase lag between the applied force and the deformation (Figure 9). All viscoelastic materials lie in between these two extremes, and shows phase lag between 0^o and 90^o.

With the help of the sinusoidal force, DMA can measure the modulus as an in-phase component: storage modulus, and as an out of phase component: loss modulus. The storage modulus is a measure of elastic behavior of material, while the ratio of the loss to storage is called tan delta, which tells us the dissipation of material, and how well a material will be at vibration energy absorption. The properties vary with the state of materials, temperature, and frequency. The phase difference between the applied stress and resulting deformation can be used to determine other fundamental parameters like complex and dynamic viscosity, transition temperature, creep, stress relaxation, as well as related performance attributes such as rate and degree of cure, sound absorption, impact resistance, and morphology [100].

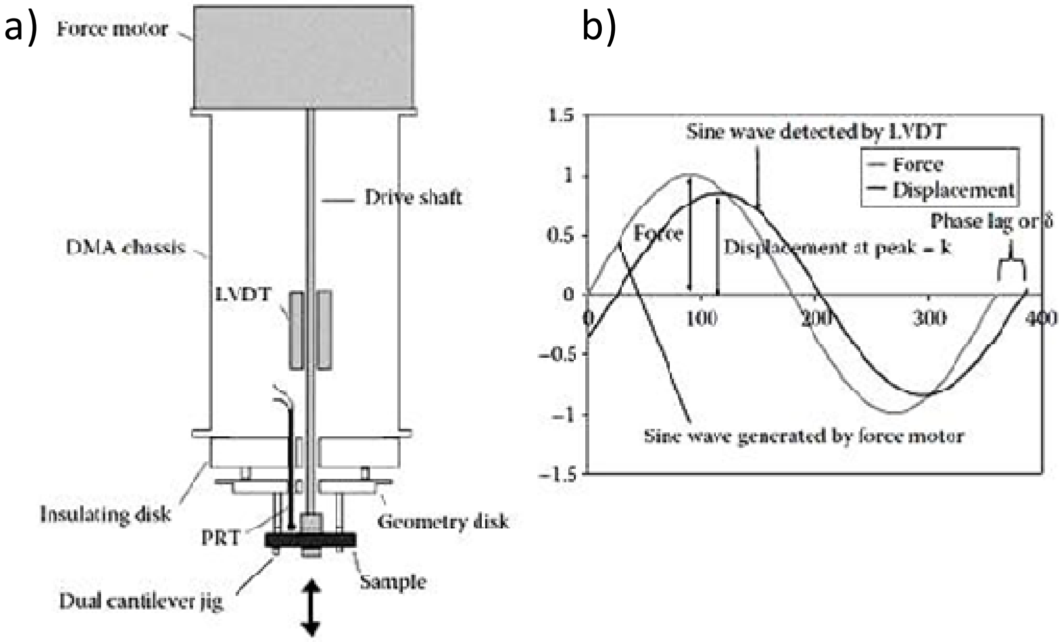

Figure 8: Working Principle of DMA: a) Schematic of PerkinElmer DMA 800, b) applied sinusoidal force and corresponding detected strain.

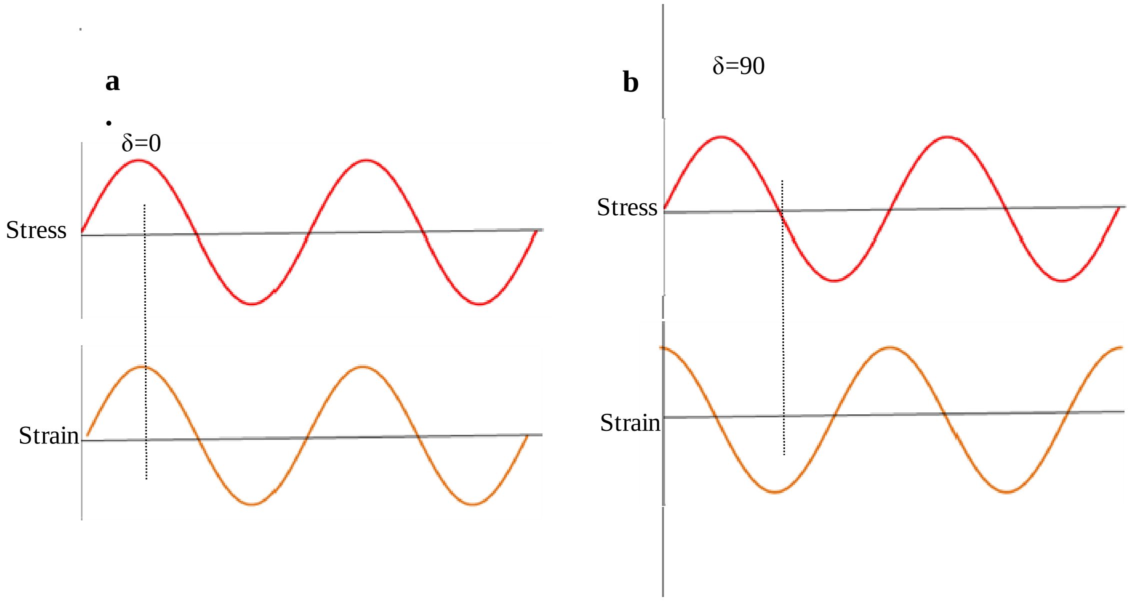

Figure 9: Response of ideal extremes: a) Purely elastic response (Hookean Solid), b) Purely viscous response (Newtonian Liquid).

3.1.2. ASTM recommendation for Dynamic Mechanical Analysis

According to ASTM standard [101], DMA practice is intended for materials having an elastic modulus range from 0.5 MPa to 100 GPa. A common assumption of this technique is the tests are conducted in the linear viscoelastic region of a material's behavior. ASTM D 4065 [101] mentioned that, specimens of any uniform size or shape can be analyzed for DMA in rectangular form. Recommended peak strain is less than 1%, and the test frequency should be from 0.01 to 500 Hz. DMA tests that are conducted over a range of temperatures, should be performed in an incremental steps or rates, slow enough to allow temperature equilibrium throughout the entire specimen. The time to reach equilibrium depends on the mass of the particular specimen, and the gripping arrangement. Generally a temperature program rate is 1-2^o C/min, or step a interval 2-5^o C, held for 3-5^{o}C minutes are found suitable. Duplicate specimens are preferred to test, and the mean results are suggested to report.

3.1.3 DMA Q800

A DMA Q800 was used for viscoelastic characterization, creep and stress relaxation tests. The DMA Q800 is the 3rd generation of DMA from TA Instruments, which offers a wide range of flexibility in choosing experimental parameters. It utilizes state-of-the-art, non-contact, linear drive technology to provide precise control of stress, and an air bearing for low friction support. Optical encoder technology is used to measure strain in the DMA Q800. General specifications of the Q800 are given in Table 2.

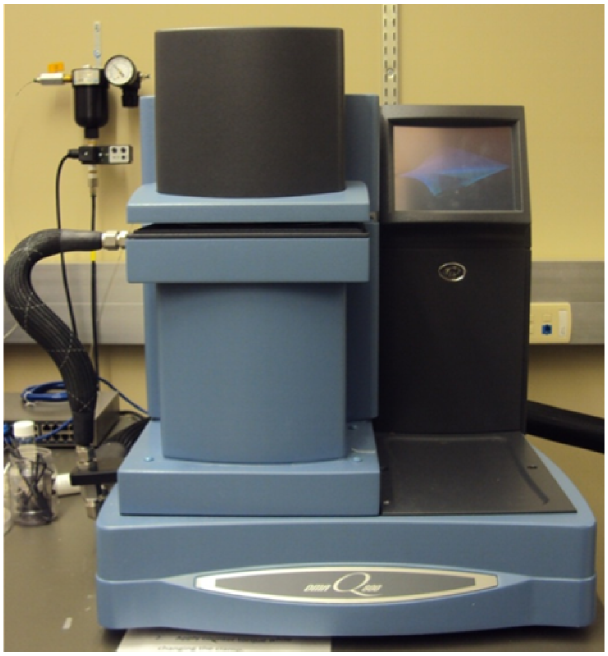

Figure 10: DMA Q800 used for experiments

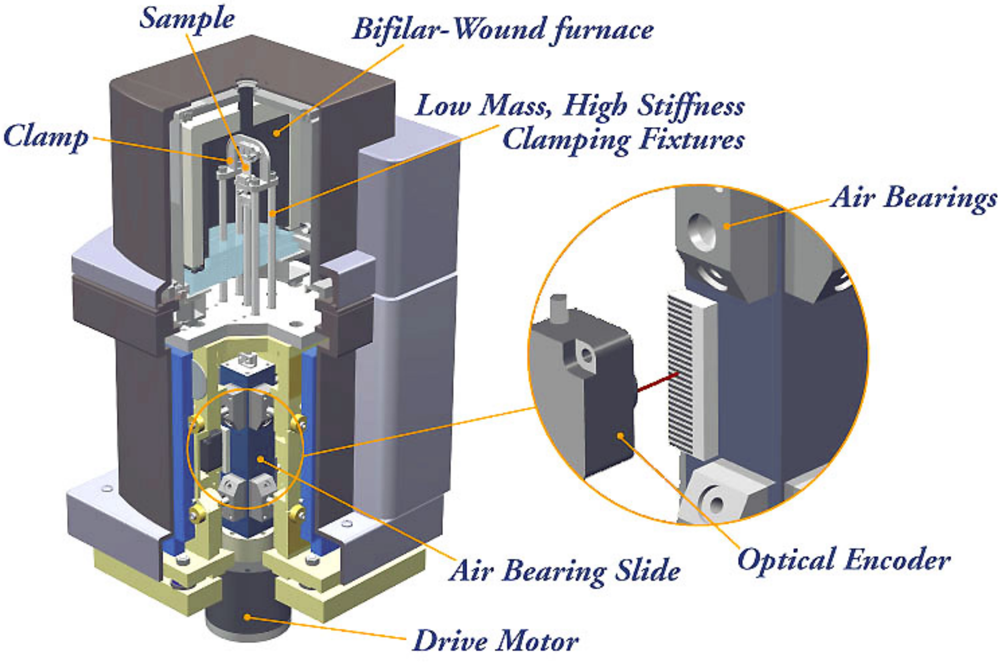

Figure 11: Schematic of DMA Q800 [102]

Table 2: Experimental Specifications of the DMA Q800 [103]

Maximum Force	18 N
Minimum Force	0.0001 N
Force Resolution	0.00001 N
Strain Resolution	10^{-9} m
Modulus Range	10^3 to 3×10^{12} Pa
Modulus Precision	±1%
Tan δ Sensitivity	0.0001
Tan δ Resolution	0.00001
Frequency Range	0.01 to 200 Hz
Dynamic Sample Deformation Range	±0.5 to 10000 μm
Temperature Range	-150 to 600 ^{o}C
Heating Rate	0.1 to 20 ^{o}C/min
Cooling Rate	0.1 to 10 ^{o}C/min
Isothermal Stability	±0.1 ^{o}C
Time/Temperature Superposition	Yes

3.1.3.1. Clamps of DMA Q800

Different types of clamps are available for the DMA Q800 to accommodate several types of samples. Selecting the appropriate clamp depends on the type of the materials, plan, and objective of the experiment and expected modes of deformation. The clamps can be classified as either tensioning clamps or nontensioning clamps [104].

Tensioning Clamps:

- 3-point bending
- Film Tension
- Compression
- Penetration
- Submersion compression
- Submersion film/fiber

Nontensioning clamps:

- Single cantilever
- Dual cantilever
- Shear sandwich

3.1.3.1.1. Tension Film Clamp

As, samples used for characterizing viscoelastic properties, creep behavior and stress relaxation of HDPE are film type; a film tension clamp was used for the experimental part of this thesis (Figure 12). It has both movable and fixed parts. The movable part was attached with the drive shaft of the stage. At first, the dovetail of the movable part slides into the dovetail holder of the drive shaft. Then the hex key tightens the setscrew in the center of the moveable part. Care has been taken not to over tighten the setscrew. Then the fixed part was attached with the mounting posts of the stage and four hex screws were tightened, enough to hold the fixed part with the mounting posts. The thermocouple was positioned in a way so that it did not touch the sample.

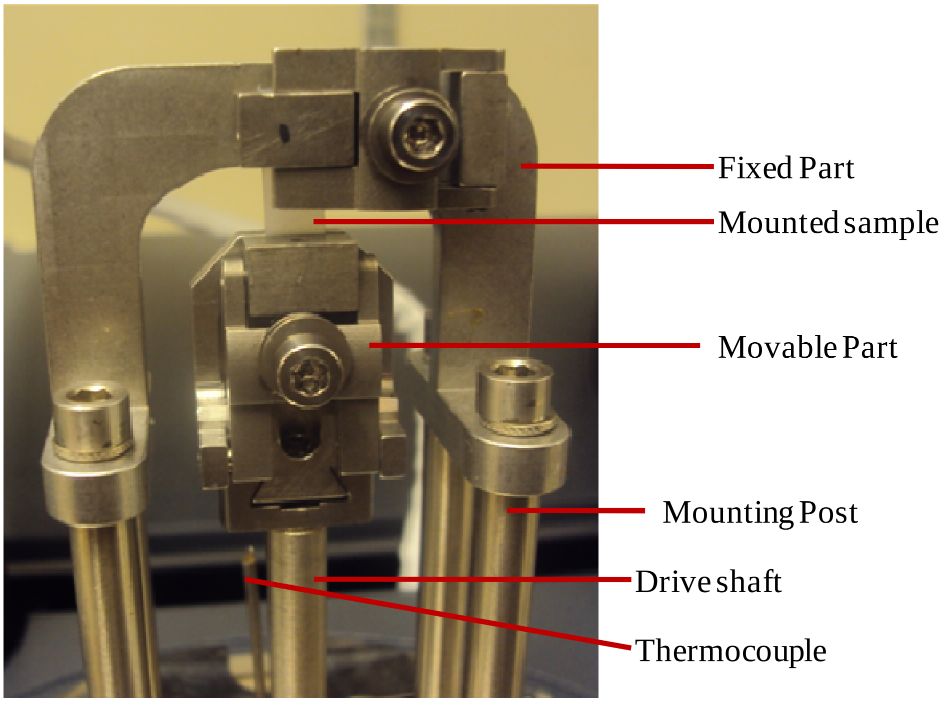

Figure 12: Film Tension clamp

3.1.3.2. Calibration of DMA Q800

Proper calibrations should be done in DMA before starting any experiment requiring precise results. . Calibration should be done periodically. A brief description of the calibration process has been described below, the details of the calibration process can be found in the online documentation accessed through the instrument control software [104].

3.1.3.2.1. Electronics Calibration

Electronic calibration is used to calibrate the instrument's electronics and drive motor over the entire frequency range of the instrument. It locks the slide (drive shaft) by automatically removing the air and applies a static force (preload force) to the motor as a calibration reference. The DMA Q800 then uses a series of frequencies to perform the calibration. Electronics calibration is recommended when the DMA Q800 is moved or at least once a month.

3.1.3.2.2. Force Calibration (Balance and Weight)

Force calibration provides the proper adjustment of the force exerted by the clamp on the samples and the force registered by the instrument as the experiment proceeds. It involves two steps: balance and weight calibration. Like the electronics calibration, force calibration should be done when the DMA Q800 is moved or at least once a month.

3.1.3.2.3. Dynamic Calibration

Dynamic calibration is used to characterize the dynamic performance of the instruments. Several samples of known stiffness are used for performing this calibration process. Dynamic calibration is needed when:

- The DMA is moved
- The feed hose for the GCA or Air Cool is either removed or installed
- At least once a month.

3.1.3.2.4. Position Calibration

The position calibration is required to calibrate the absolute position of the drive shaft (and slide) as read by the optical encoder. The position calibration should be done when the calibration is lost, the instrument is moved, or at least once a month.

3.1.3.2.5. Clamp Calibration

Clamp calibration helps the instrument with the specific properties of particular clamp installed on the stage. Clamp calibration involves three steps: Mass calibration, zero calibration, and compliance calibration. This calibration should be done every time when the clamp is changed.

3.1.4. Sample used for DMA Q800

3.1.4.1. HDPE-$CaCO_3$ Composites

$CaCO_3$ was incorporated in HDPE to investigate the change of time dependent properties. Omayacarb FT-FL were used as a source of $CaCO_3$. Omayacarb FT-FL contains high purity, fine, wet ground, and surface-treated natural calcium carbonate. It can be used as an additive in food packaging applications under 21 CFR (FDR) 174.5, 175.300 and 178.3297. However Omayacarb FT-FL is not qualified as a substance, permitted for direct addition to human food or animal feed. The specification of Omayacarb FT-FL can be found elsewhere [105]. Major applications of HDPE are in packaging industries, and properties of polymers depend on processing conditions. Therefore to compare, how HDPE will behave in end products, samples were collected from industrial scale equipment. 1.9 L (0.5 gal) bottles were blow molded with increasing weight fractions of $CaCO_3$ in HDPE. Samples used for experiments were cut from these bottles. Figure 13 shows a parallel cutter, which was used to ensure uniform width of the samples. Four different weight fractions of $CaCO_3$ were compared for the viscoelastic, creep and stress relaxation experiments. They were:

- 0%(Neat) $CaCO_3$-HDPE
- 5% $CaCO_3$-HDPE
- 10% $CaCO_3$-HDPE
- 20% $CaCO_3$-HDPE

Figure 13: Parallel cutter used to ensure uniform width of the samples.

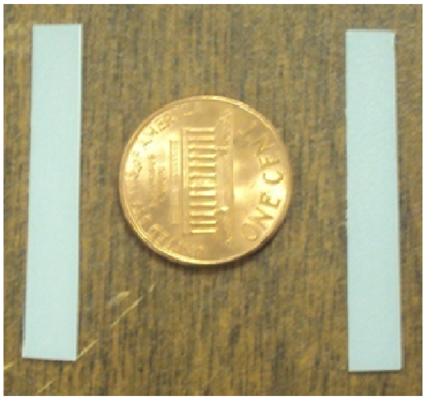

Figure 14: HDPE-$CaCO_3$ composite samples used in DMA.

3.1.4.2. Neat HDPE from Closure

Another significant application area of HDPE is in closures, (caps). HDPE closures are frequently used in beverage packaging industries for bottles made with PET. Light weighting closures approaches limits in industry, like low seal failure load over long periods. This necessitates the analysis of viscoelastic properties of HDPE used in closures. As Injection molding offers ultimate part design flexibility, consistency with preform molding, and good tolerance in the final products; it is replacing some other manufacturing processes (such as compression molding) in closure industries. For characterizing HDPE behaviors in ageing and annealing, neat HDPE was collected from caps, manufactured by the injection molding. A HUSKY 300 (Figure 15) was used for injection molding, and the caps were collected immediately after injection molding when they came out of the mold (Figure 16). Then, with the parallel cutter, a rectangular strip of neat HDPE was cut from the cap as shown in Figure 17.

Figure 15: Caps were collected from Husky 300 Injection molding machine.

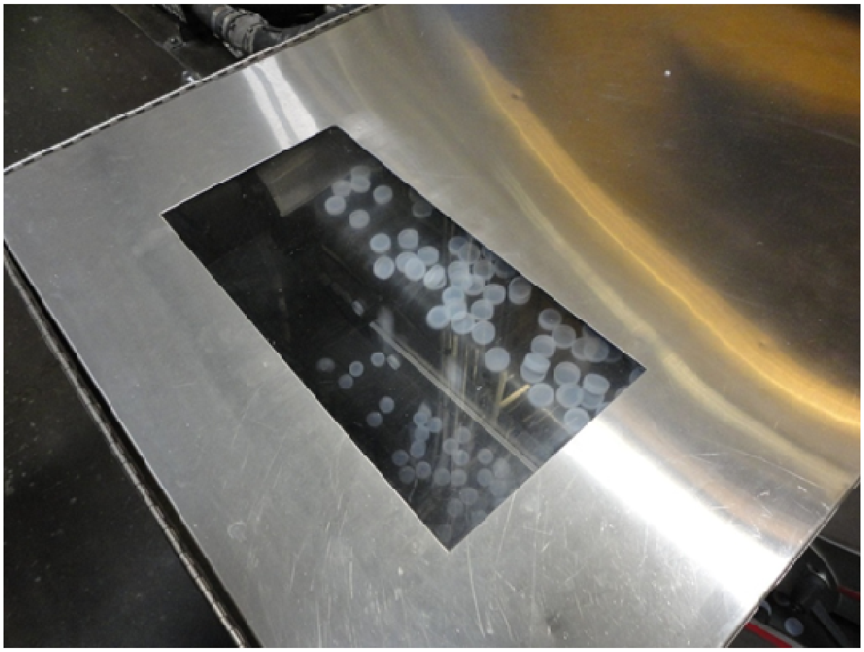

Figure 16: Caps were collected just after the mold of injection molding machine.

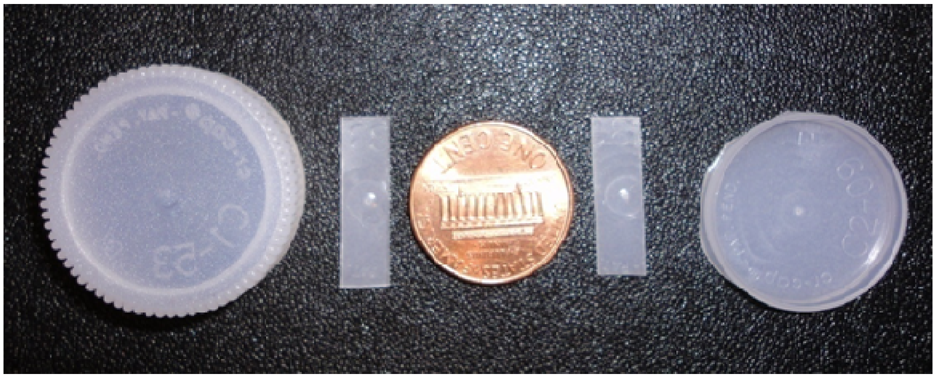

Figure 17: Neat HDPE samples (center strips) cut from closures for ageing and annealing tests.

3.1.5. Tests and Parameters

Different modes of tests were conducted on HDPE-$CaCO_3$ composites, and on neat HDPE collected from closures to investigate viscoelastic properties, creep behavior, stress relaxation, ageing, and annealing effects on HDPE. The following section includes detail description of the tests conducted, and parameters used in different types of tests.

3.1.5.1. HDPE-$CaCO_3$ Composites

Stress Strain

Stress strain curves were generated by these experiments. The stress strain curves give an idea about the linear viscoelastic range of HPDE. Generally rheological tests are recommended to conduct within the viscoelastic range of the material. Stress strain curves generated by these experiments were used to get the linear viscoelastic range and to measure the modulus of the HDPE-$CaCO_3$ composites.

Viscoelasticity

Viscoelastic properties were characterized in two different ways: as a function of frequency and as a function of temperature. These tests are important to identify the transition points of the polymers. The parameters used in the DMA for these tests are given below:

As a Function of Temperature:

Mode: Multi-Frequency – Strain

Test: Temperature Ramp-Frequency sweep

Clamp: Tension film

Amplitude: 15μm

Static Force: 0.0100

Soak time: 5 min

Force track: 125%

Temperature range: 25 to 115^{o} C

Ramp rate: 3.00 °C/min

As a Function of Frequency:

Mode: DMA Multi-Frequency – Strain

Test: Isothermal frequency sweep

Clamp: Tension film

Amplitude: 15 μm

Static Force: 0.0100

Force Track: 125.0 %

Frequency range: 0.1 to 100 Hz

Temperature: 30^{o}C

Creep Tests

Two different types of creep tests were performed with different parameters.

Short Term Creep and Recovery Test

Short term creep and recovery tests were performed within linear viscoelastic range of HDPE. Linear viscoelastic range was determined from stress strain curves. 10 minutes creep and 20 minutes recovery tests were conducted at 0.5 MPa static force to observe creep performance of HDPE-$CaCO_3$ composites within the viscoelastic range. The parameters for the tests are given below:

Mode: DMA Creep

Test: Creep

Clamp: Tension film

Creep stress: 0.5 MPa

Static Force: 0.001 N

Temperature: 30^{o}C

Soak time: 5 min

Creep time: 10 minutes

Recovery time: 20 minutes

Long Term Creep and Recovery Test

In reality, products made with HDPE experience loads much higher than the loads in the linear viscoelastic range. Moreover the products are subjected to load over long times. For these reasons, to mimic the practical case, higher static stress and longer time periods are necessary for studying the creep behavior. With the available geometry of samples, maximum 5.5 MPa static stress was possible to exert on the samples due the limitation of maximum load (18 N) available in DMA Q800. These higher stress creep tests were conducted over 12 hour period. 3 Samples from each type of composites (0%, 5%, 10%, and 20%) were tested to investigate the distribution of results from DMA Q800. The parameters used for the tests are:

Mode: DMA Creep
Test: Creep
Clamp: Tension film
Creep stress: 5.5 MPa
Static Force: 0.001 N
Temperature: 30^{o}C
Soak time: 5 min
Creep time: 720 minutes
Recovery time: 0 minutes

Stress Relaxation Test

ASTM standard recommends, strain should be less than 1% for Dynamic Mechanical Analysis of materials [101]. Strain rate of 0.8% was selected for the stress relaxation tests. 3 samples for each type of composites (0%, 5%, 10%, and 20%) were tested for stress relaxation experiments to have a better idea of the distribution of the stress among different types of composites. All the tests were performed for 240 minutes. The parameters used for the stress relaxation tests are:

Mode: DMA Stress Relaxation
Test: Stress Relaxation
Clamp: Tension film
Displace: 0.8%
Static Force: 0.001 N
Temperature: 30^{o}C
Soak time: 5 min
Displace time: 240 minutes

3.1.5.2. Neat HDPE from Closure

Effect of ageing and annealing were investigated on samples on neat HDPE samples collected from injection molded caps. For characterizing ageing effects on fresh HDPE, a bunch of caps were collected just after the injection molding process (Figure 16), and short term stress relaxation tests were performed after increasing lengths of time about 15 to 30 min each, as indicated in the results section. Two different annealing parameters were used to investigate the effect of annealing on two sets of samples. The first set was annealed at 125^{o}C for 30 minutes and the second set was annealed at 125^{o}C for 1 hours. Both sets were then air cooled bringing them out of the furnace after designated time period. Then both sets were subjected to short term stress relaxation tests after increasing lengths of time about 15 to 30 min. These types of tests also give an idea about the effect of ageing on annealed samples. For annealing, a Memment model UNB 400 Oven from Wisconsin Oven Distributors, LLC was used. As an initial trial, a set of caps were set at 140^{o}C for 1 hour but all the caps were found completely melted.

Stress Relaxation tests parameters for aged and annealed samples

Mode: DMA Stress Relaxation

Test: Stress Relaxation

Clamp: Tension film

Displace: 0.9%

Static Force: 0.1 N

Temperature: 30^{o}C

Soak time: 1 minute

Displace time: 15 minutes or 20 minutes

3.2. Density of HDPE-CaCO$_3$ composites

The density of HDPE-CaCO$_3$ composites was measured by the Archimedes principle. At first, the weight of the composite samples was measured using a XS204 Deltarange from Mettler Toledo. Then the composite samples were immersed into methanol and using the same balance, their weights in methanol were measured. Then using the following formula, the density of the composites with different weight fraction of $CaCO_3$, was calculated.

$$\text{Density of HDPE-CaCO}_3 = \frac{Weightinair}{Weightinair - Weightinmethanol} \times \text{Density of Methanol}$$

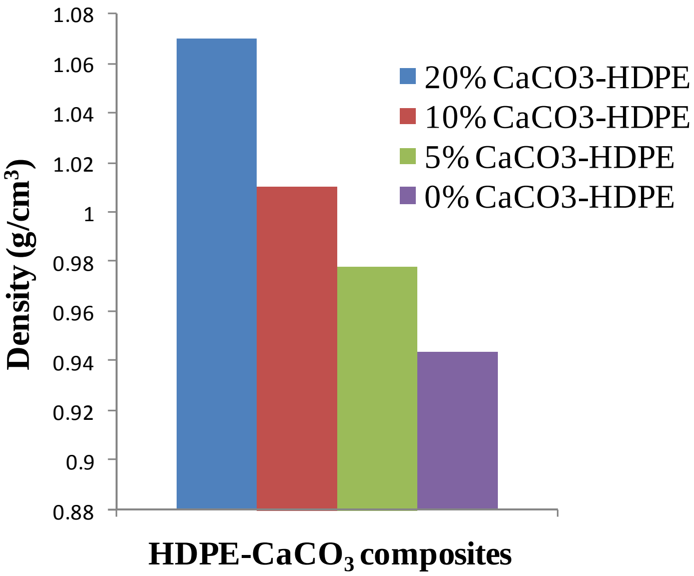

Figure 18: Density of HDPE-$CaCO_3$ composites

3.3. Seal Failure from Squeeze Pressure

Seal failure, from squeeze pressure is a critical parameter for measuring the performance of bottles. Here, seal failure load refers to the compressive load on the side walls of the bottles required to observe leakage. There is not yet an accepted standard for measuring this property.

Leakage can be observed at different points depending on the design. Leakage near the seal of the cap is more common. Leakage can also be observed at the injection gate on the base of the bottle. Due to its importance in industry, different available bottles were collected, and their seal failure loads and sidewall stiffness were investigated.

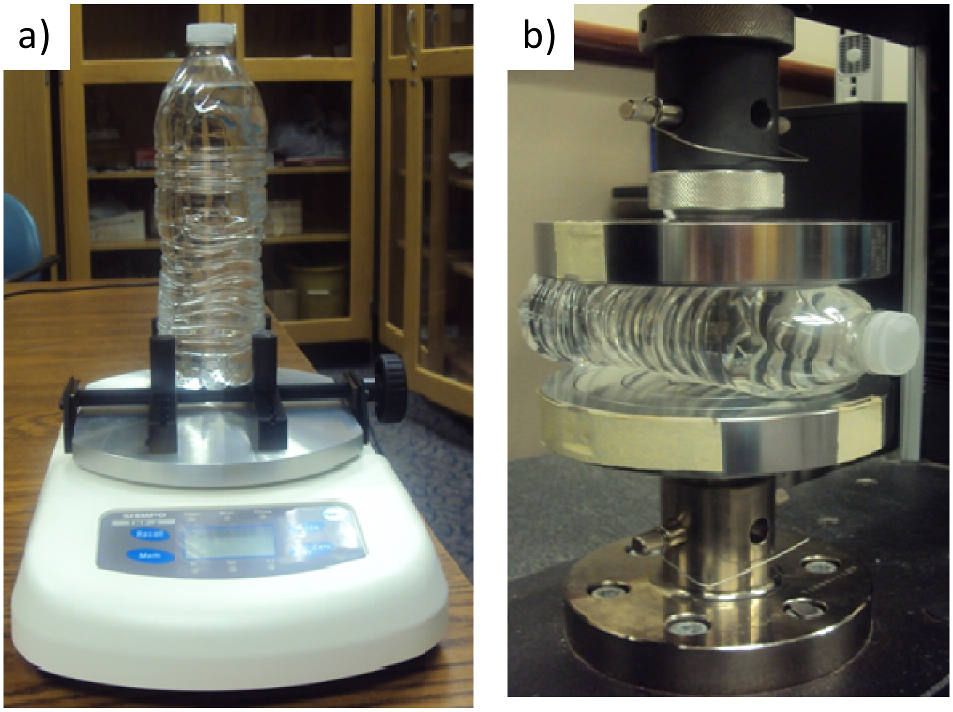

Figure 19: a) Shrimpo TNP Torque Meter b) Seal failure testing in Mechanical Tester

3.3.1. Methods

12 different types of 0.5 liter water bottles were collected with different designs. For each type of bottle, at least three samples were tested for seal failure. Failure loads were measured using an INSTRON 5582 universal testing machine. Compression testing mode with a compression rate of 10 mm/min was used with 15.24 cm (6 inch) diameter compression platen shown in the Figure 19. Compressive loads were applied by the

machine until the first drop of water came out from the bottle. For most bottles, leakages were observed near the seal of the caps. However, some bottles did not leak at the cap. They leaked in the base, near the injection gate of the bottle (Figure 20). Few bottles were observed to burst instead of leaking. Bottles that burst instead of leaking showed the most load reported in the results and discussion section. Almost all types of the bottles used for seal failure testing were automatically capped. Two particular types of bottles were manually capped, monitored by a Shrimpo TNP torque meter with a torque range of 1.13 +/-0.12 N-m (10 +/-1 in-lb) (Figure 19).

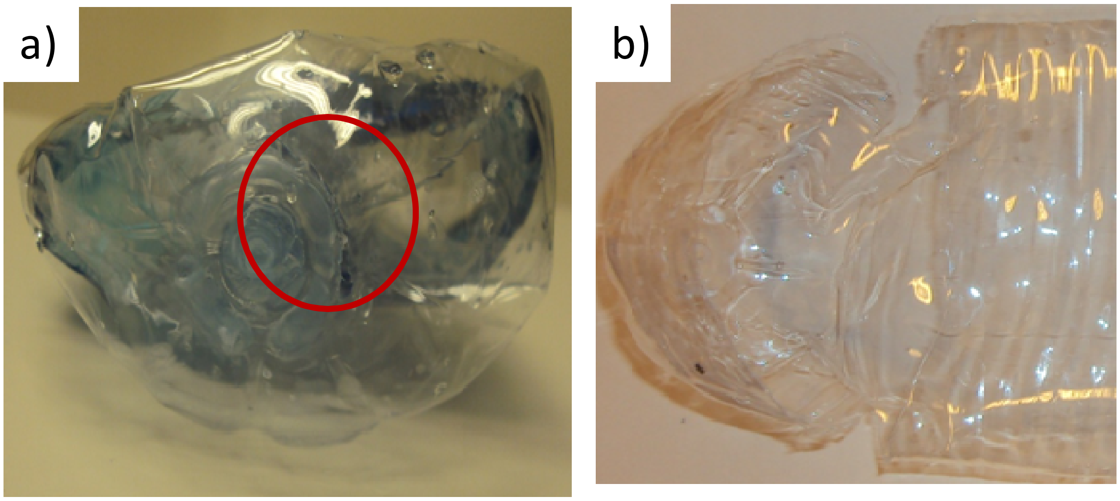

Figure 20: Failure of water bottles; a) leaking in the base, b) bursting of side walls

CHAPTER IV

4. RESULTS AND DISCUSSION

4.1. HDPE-$CaCO_3$ Composites

4.1.1. Stress Strain curves for HDPE-$CaCO_3$

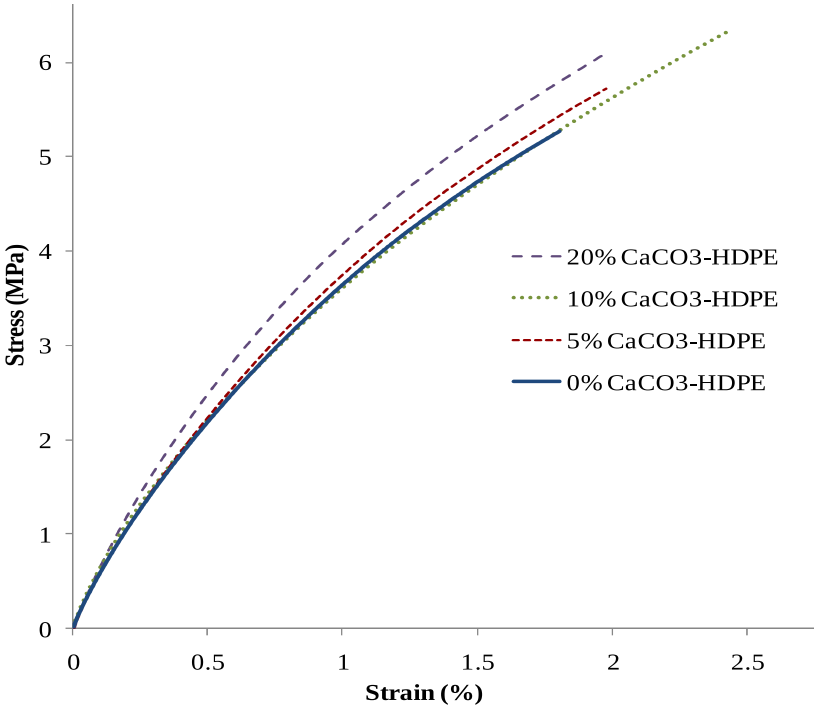

Figure 21: Stress strain curve of HDPE with Calcium Carbonate.

Figure 21 shows some effects of $CaCO_3$ on the constitutive response of HDPE. The stress strain curve for 10% $CaCO_3$-HDPE composite almost coincides with the stress strain curve for the control HDPE. The stress strain curve for 20% $CaCO_3$-HDPE confirms the expected increase in modulus with increasing $CaCO_3$ content in HDPE. At low strain levels (0.25% strain), 20% $CaCO_3$-HDPE showed a 14%[1] increase in the modulus over 0% $CaCO_3$-HDPE. The stress stain curves are important to find the linear viscoelastic region of stress and strain for HDPE.

4.1.2. Viscoelastic properties

Viscoelastic properties of HDPE-$CaCO_3$ composites have been studied as a function of temperature, and as a function of frequency.

4.1.2.1. As a Function of Temperature

Figure 22 and Figure 23 shows the storage modulus as a function of temperature. Storage modulus was observed to increase by addition of $CaCO_3$ in HDPE. At 30^o C, the storage modulus increased around 23%[2] for the 20% $CaCO_3$ HDPE composite over the control HDPE. No significant change of storage modulus was observed by increasing $CaCO_3$ weight fraction from 5% to 10%. Figure 22 and Figure 23 depict that, incorporation of $CaCO_3$ increases storage modulus more at lower temperature than at higher temperature (at 100^{o}C, storage modulus was observed to increase by 12%[3] in 20%

---

[1] ((1.47MPa-1.269 MPa)/1.269 MPa×100)

[2] ((1395MPa-1135MPa)/1135 MPa ×100)

[3] ((240 MPa-215 MPa)/215 MPa)×100

$CaCO_3$-HDPE composite than the neat HDPE). Figure 24 shows the loss modulus at different temperatures in $CaCO_3$-HDPE. Incorporation of $CaCO_3$ also increased the loss modulus in HDPE. Like storage modulus, no significant change of loss modulus was observed by increasing $CaCO_3$ weight fraction from 5% to 10%. The addition of $CaCO_3$ did not show significant change of the tan delta at different temperature (Figure 25). At 30°C, only 0.30%[4] increase in tan delta was observed by increasing $CaCO_3$ content from 0% to 20%.

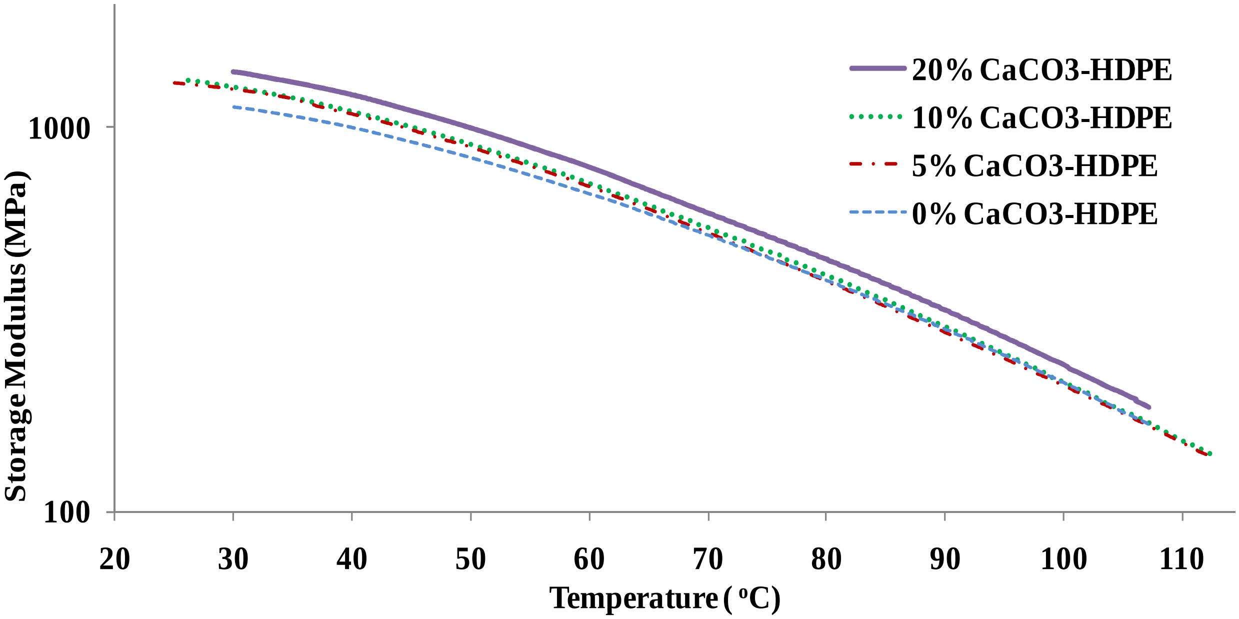

Figure 22: Storage Modulus of different $CaCO_3$-HDPE composites as a function of temperature (Log scale)

---

[4] ((0.122742-.0122366)/0.122366)×100

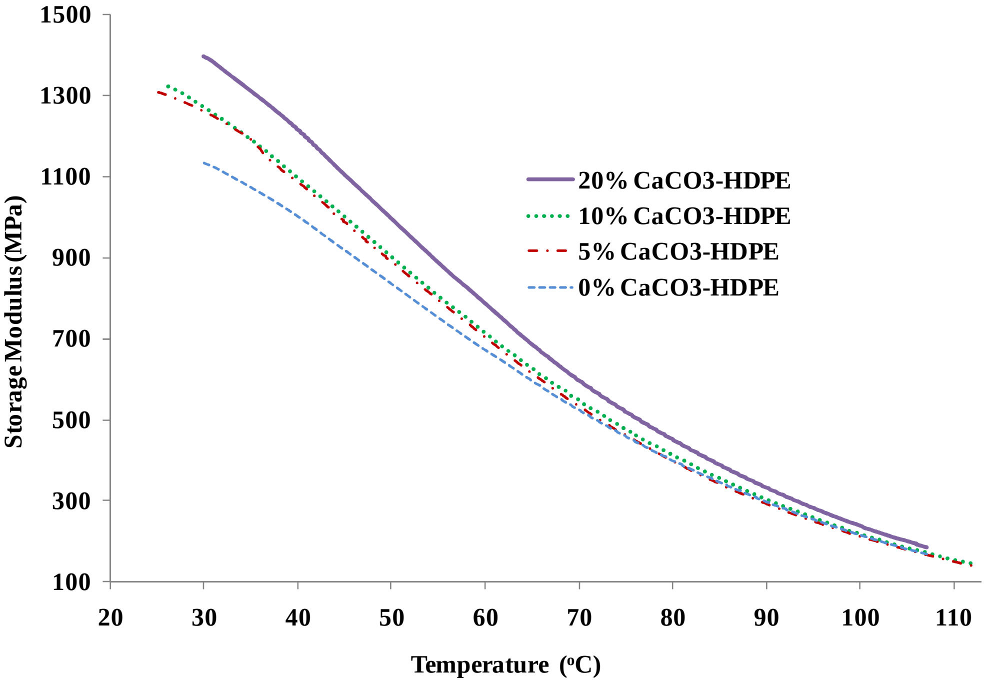

Figure 23: Storage modulus as a function of temperature (Normal scale)

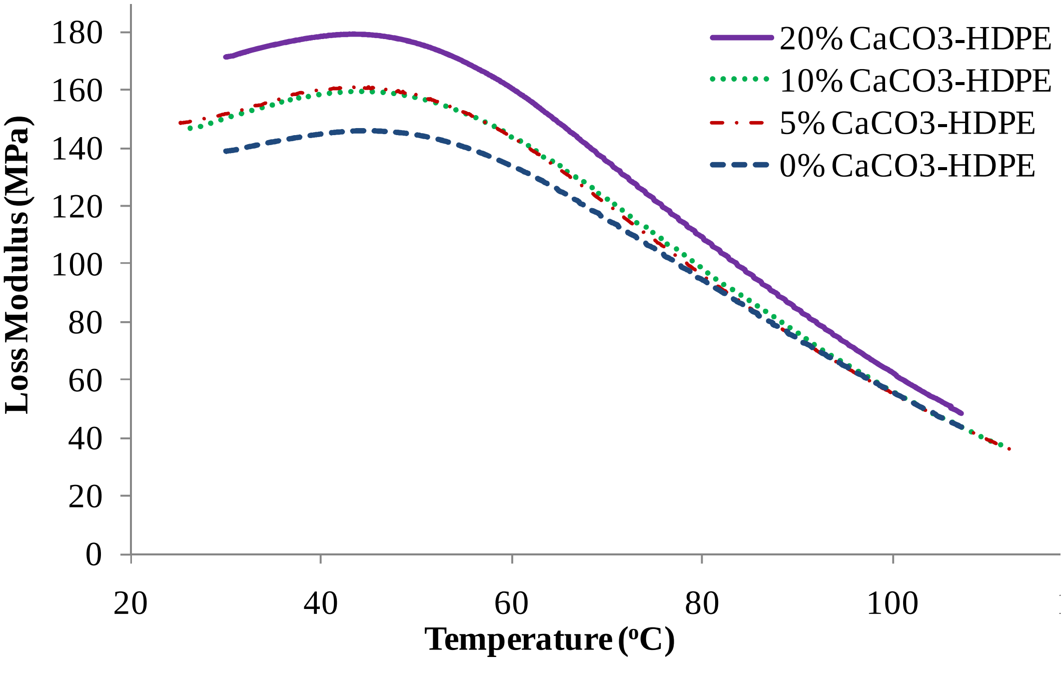

Figure 24: Plot of Loss Modulus as a function of temperature in different $CaCO_3$-HDPE composites

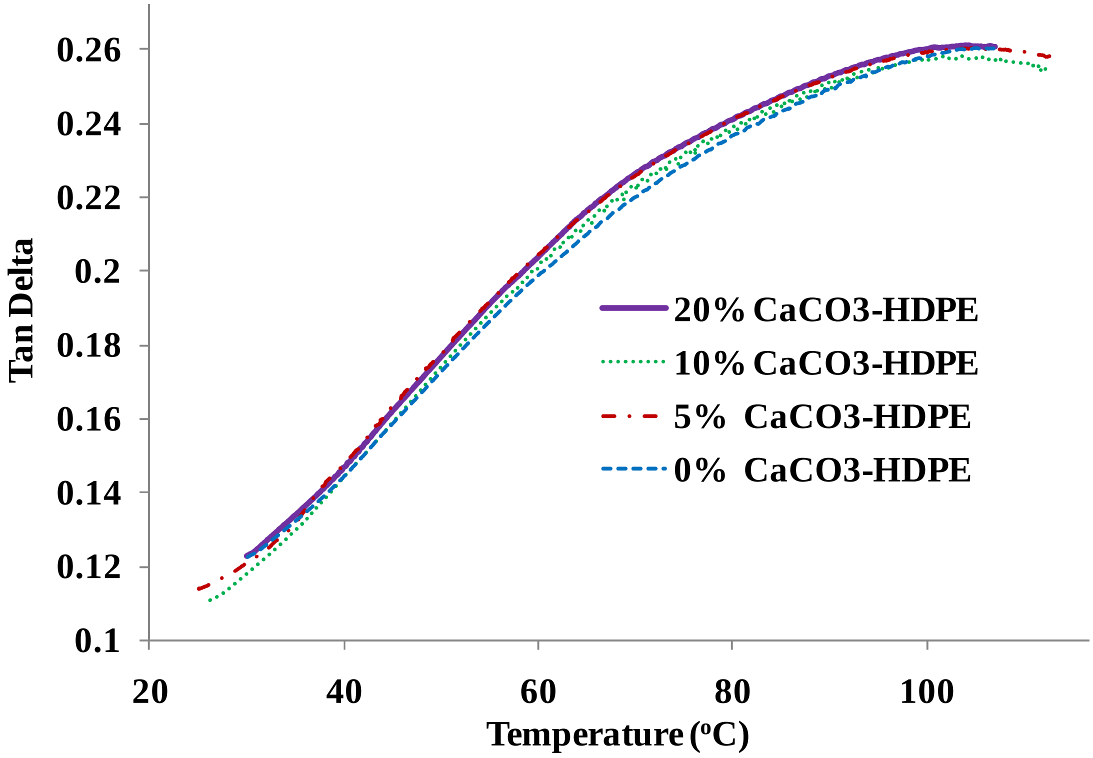

Figure 25: Plot of tan delta as a function of temperature in $CaCO_3$-HDPE composites

The results found from the viscoelastic properties vs. temperature tests confirm the findings of Yang *et al.* [59]. They also observed a significant increase in storage modulus but very little effect on tan delta, by addition of $CaCO_3$ in HDPE. As tan delta is a measure of the dissipation of energy in materials under cyclic loading [106], it can be stated that incorporation of $CaCO_3$ does not improve the vibration energy damping ability of HDPE.

4.1.2.2. As a Function of Frequency

Viscoelastic properties of HDPE-$CaCO_3$ composites were also investigated as a function of frequencies at 30°C temperature. Figure 26, Figure 27 and Figure 28 show the storage modulus and tan delta as a function of frequencies in composites, with increasing weight fraction of $CaCO_3$. Only the 20% $CaCO_3$-HDPE composite showed a significantly higher storage modulus than the control HDPE at different frequencies. At 40 Hz, 20% $CaCO_3$-HDPE showed 16%[5] increase in storage modulus than the 0% $CaCO_3$-HDPE. Only one set of samples were tested to investigate the viscoelastic properties of HDPE-$CaCO_3$ composites. However, more sets of sample would provide better statistics about the dispersion of the properties among different types of composites.

---

[5] ((1515 MPa-1308 MPa)/1308 MPa×100)

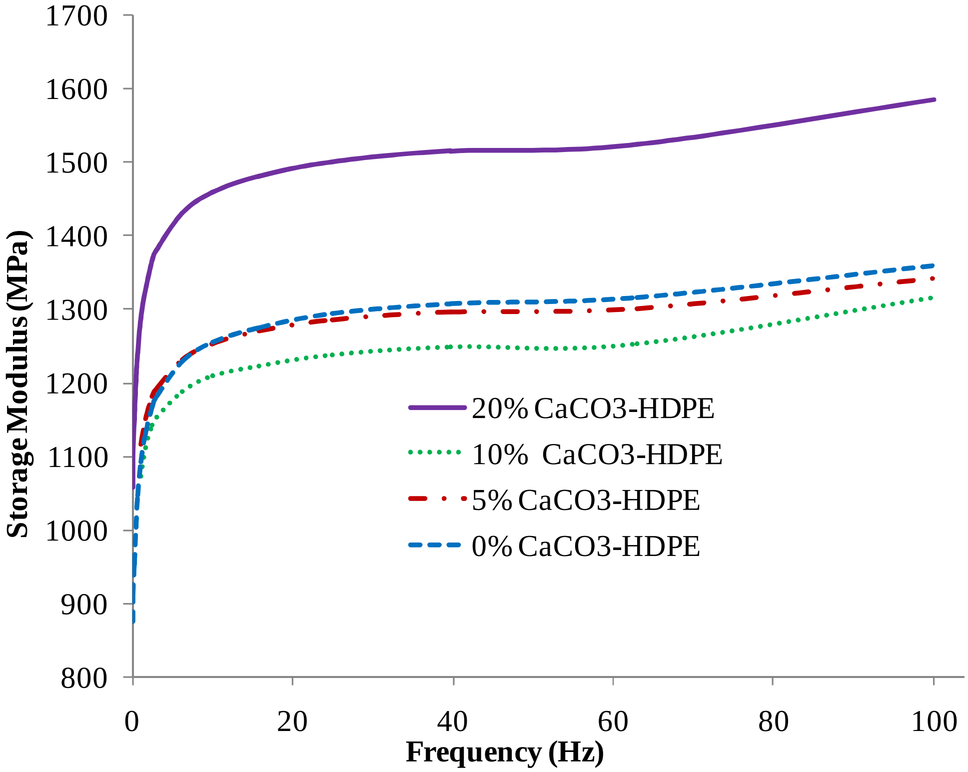

Figure 26: Storage Modulus of HDPE-CaCO$_3$ composites as a function of frequency (normal scale)

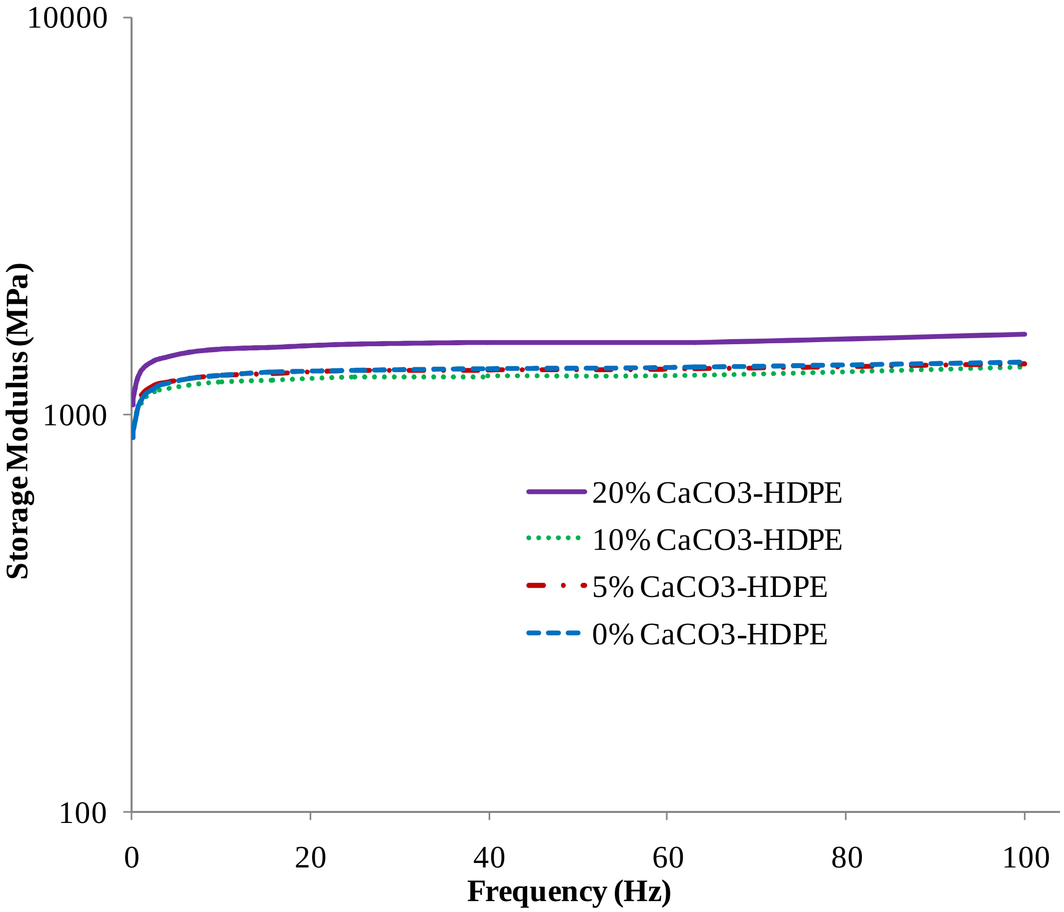

Figure 27: Storage Modulus of HDPE-CaCO3 composites as a function of frequency (log scale)

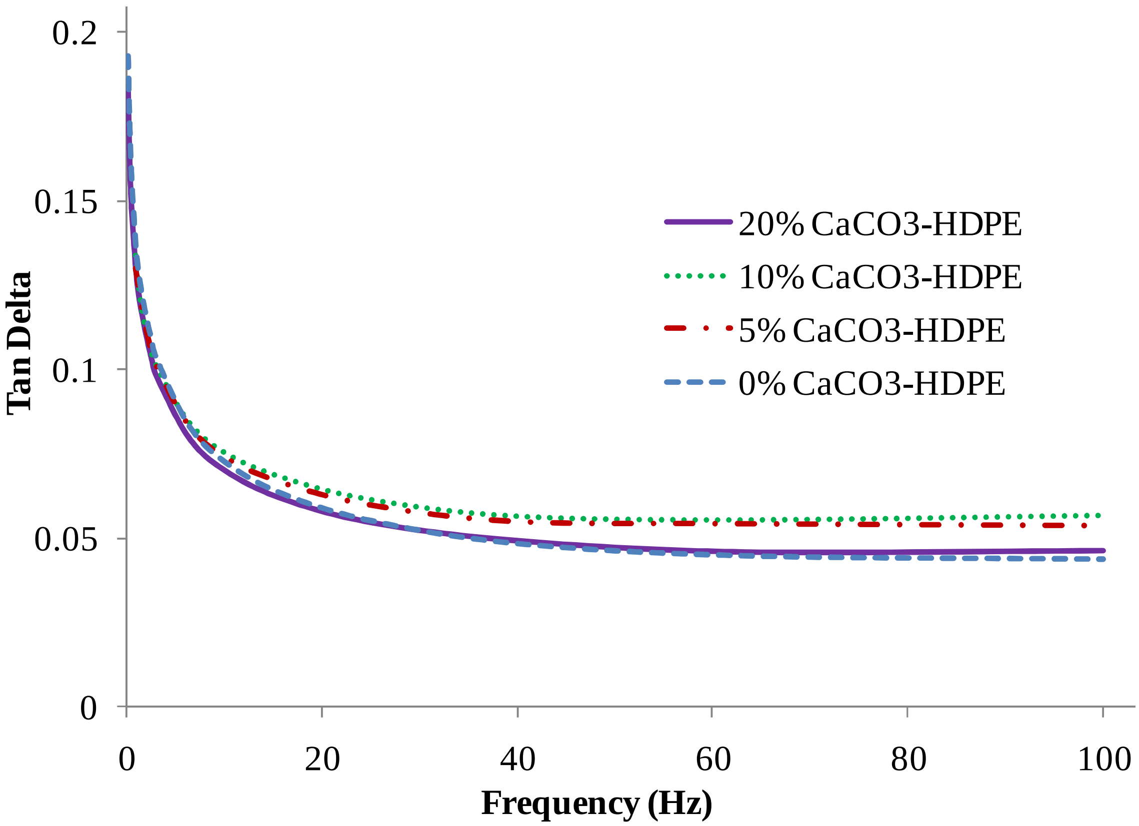

Figure 28: Plot of Tan Delta as a function of frequency

4.1.3. Creep Behavior

Creep behavior of HDPE-$CaCO_3$ composites was investigated both in linear and non-linear viscoelastic ranges. Creep experiments were conducted in two categories: Short term creep and Long term creep.

4.1.3.1 Short Term Creep

Short term creep tests were performed to observe creep behavior of the composites in the linear viscoelastic range. Figure 29 shows the creep compliance curves for HDPE-$CaCO_3$ composites. Figure 30 represents the creep, and recovery strain for the composites as a function of time. Both figures show significant improvement of the creep behavior of HDPE, by adding 20% weight fraction of $CaCO_3$. Interestingly, the creep and recovery strain for the 10% $CaCO_3$-HDPE was found higher than that of 5% $CaCO_3$-HDPE.

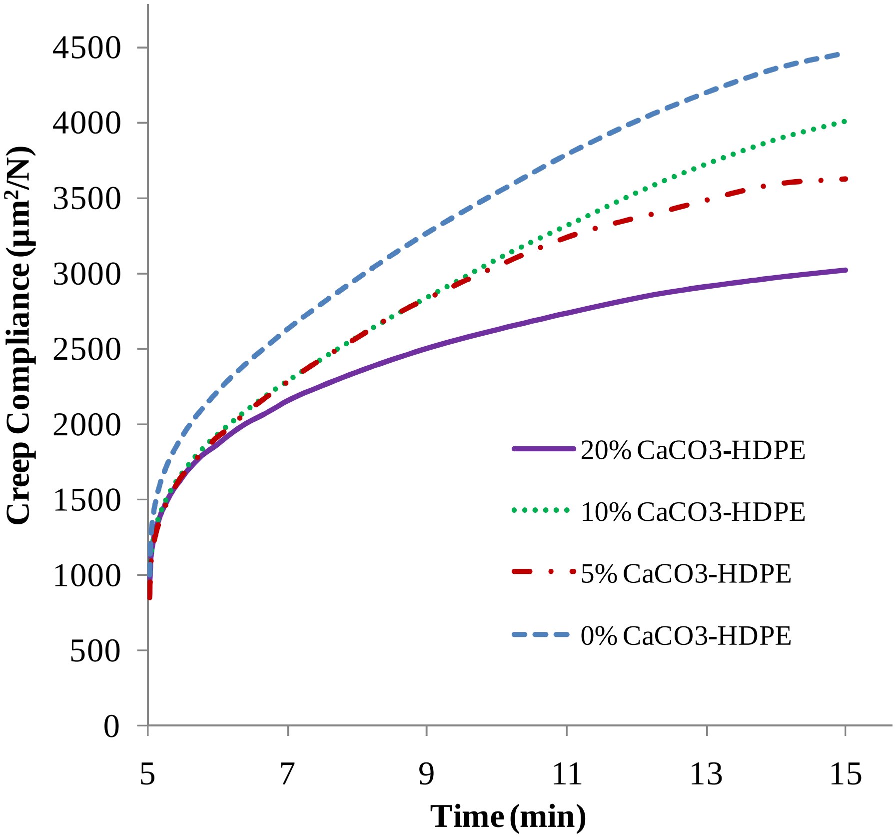

Figure 29: Plot of Creep Compliance vs. Temperature in HDPE- $CaCO_3$ composites.

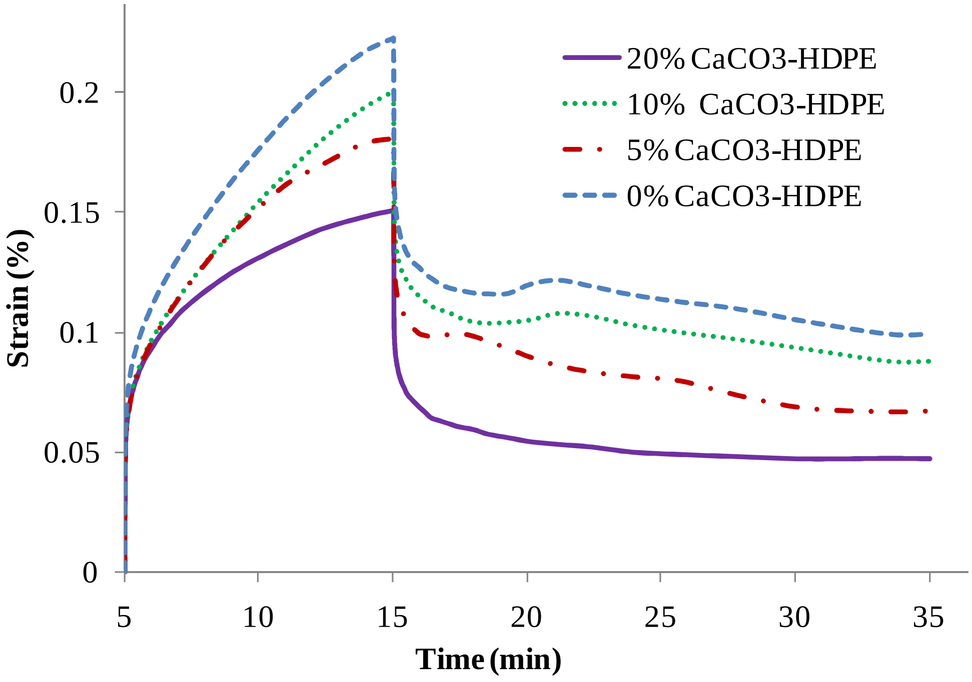

Figure 30: Plot of creep strain as a function of temperature in HDPE-CaCO$_3$ composites.

Figure 29 and Figure 30 only depict the primary region of the creep curves. Creep time and recovery time should be increased to get the secondary steady state region of the creep curve for better understanding of the creep behavior of the composites. Moreover, in practical life, products made with HDPE are subjected to much higher loads, which generate stress, outside the linear viscoelastic region of HDPE. All these reasons provoked us to conduct long term creep experiments as part of this thesis.

4.1.3.2 Long Term Creep

Figure 31 shows the individual creep strain vs. time curves for the composites over a 12 hour period. For the 5% and 20% CaCO$_3$-HDPE composites, the variation of creep strain among different samples was much less, compared to the 0% and 10% $CaCO_3$-HDPE composites. Reduced creep strain was observed for 20% $CaCO_3$-HDPE composites. Figure 32 shows the average (3 samples) creep strain curve for HDPE-$CaCO_3$ composites. Average creep strain for the 10% $CaCO_3$-HDPE composite was found slightly higher (after 12 hours, only 2%[6]) than the creep strain for the 5% $CaCO_3$-HDPE composite. The 5% and the 10% $CaCO_3$-HDPE composites also showed similar viscoelastic properties. Figure 33 depicts the average creep strain of the composites after 12 hours. Error analysis was based on the standard deviation of the values for the each sample set.

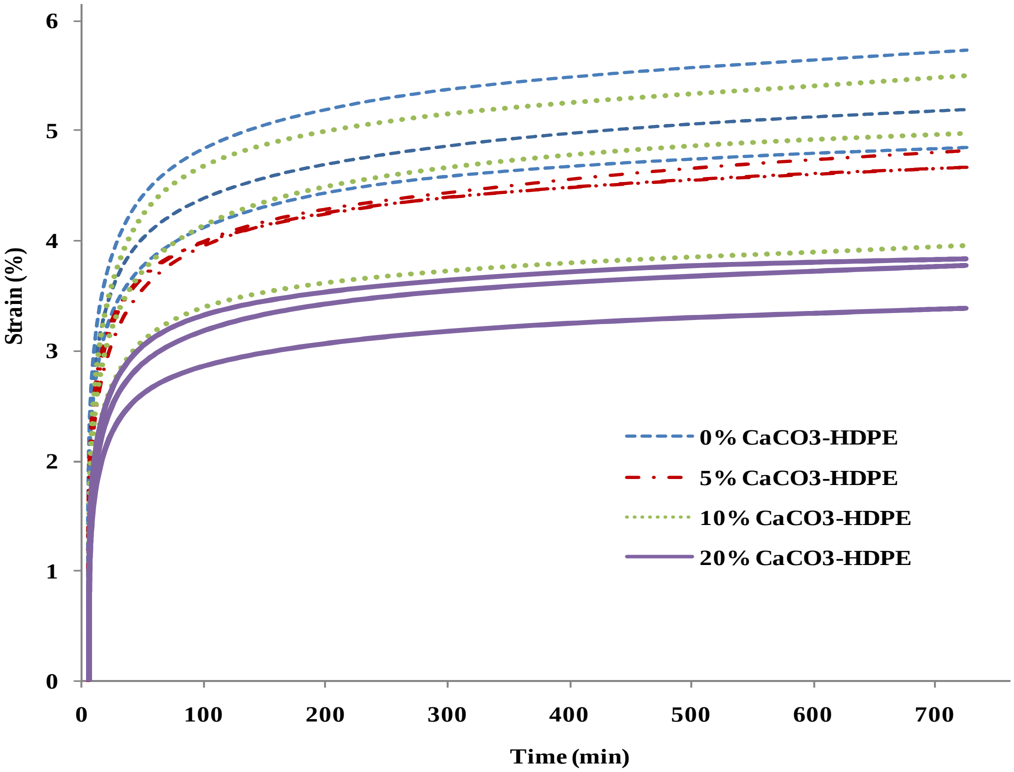

Figure 31: Plot of individual creep strain vs. time curve at 5.5MPa static stress

---

[6] ((4.80-4.70)/4.70)×100

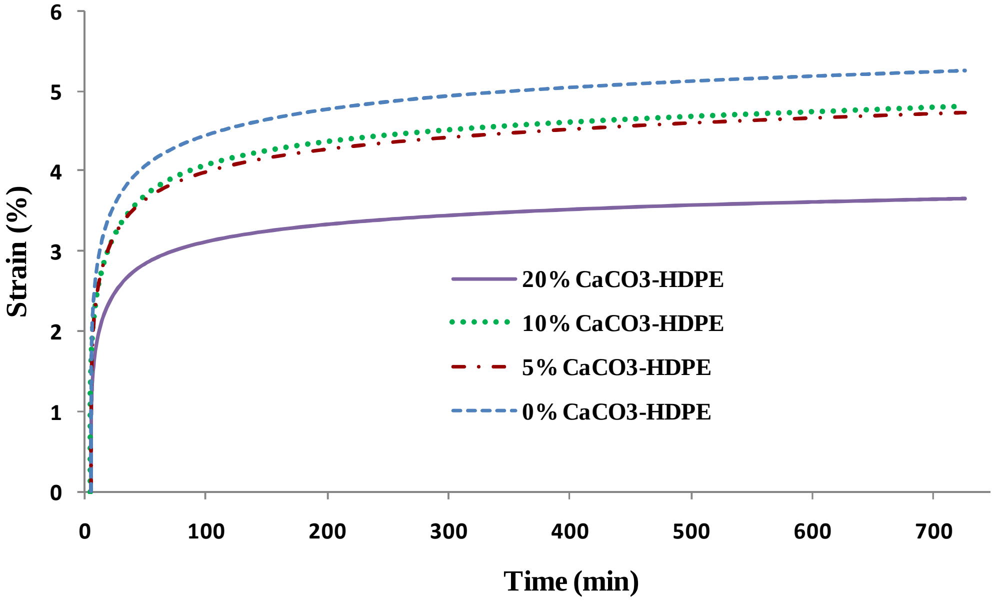

Figure 32: Average creep strain vs. time curves for HDPE-CaCO$_3$ composites at 5.5 MPa static stress

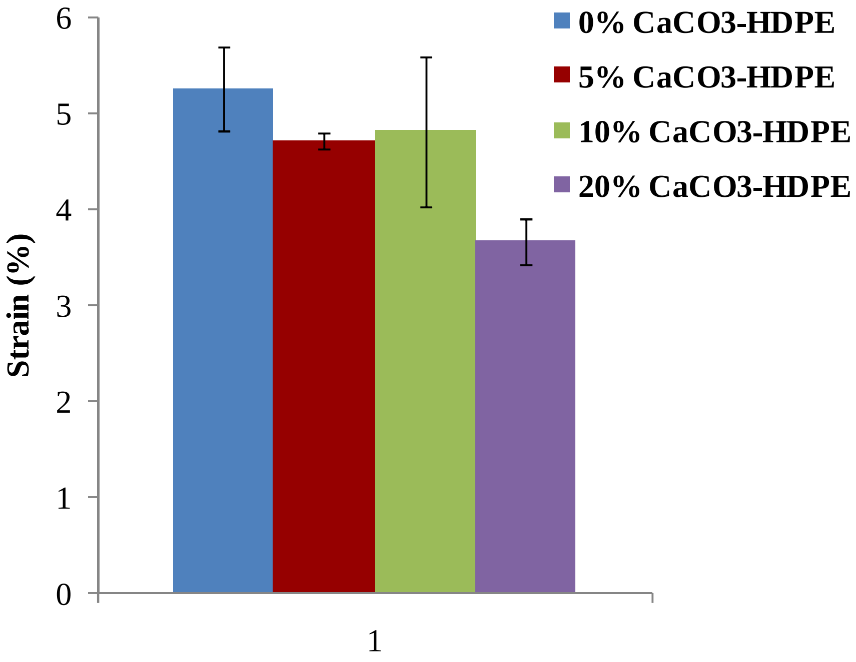

Figure 33: Average creep strain after 12 hours at 5.5 MPa static stress

After 12 hours, the average creep strain for the 20% $CaCO_3$-HDPE composite was found 30%[7] lower than the average creep strain of the control HDPE. The low creep strain in 20% $CaCO_3$-HDPE can be explained by the interpretation of Ek *et al*. [54]. They interpreted that, structural changes of the polymer around $CaCO_3$ restrict the macroscopic flow of the polymer, and as a result, low creep strain is observed for higher filler contents in the composites.

4.1.4. Stress Relaxation

Figure 34 shows the individual relaxation modulus vs. time curve for HDPE-$CaCO_3$ composites. The data show a higher value of relaxation modulus for the 20% $CaCO_3$-HDPE than the relaxation modulus of the other 3 types of samples. Figure 35 shows the average (of 2 samples) relaxation modulus vs. time curves for the HDPE-$CaCO_3$ composites. Figure 36 shows the average (3 samples) relaxation modulus of the composites after 240 minutes.

---

[7] $((5.25-3.65)/5.25)\times 100$

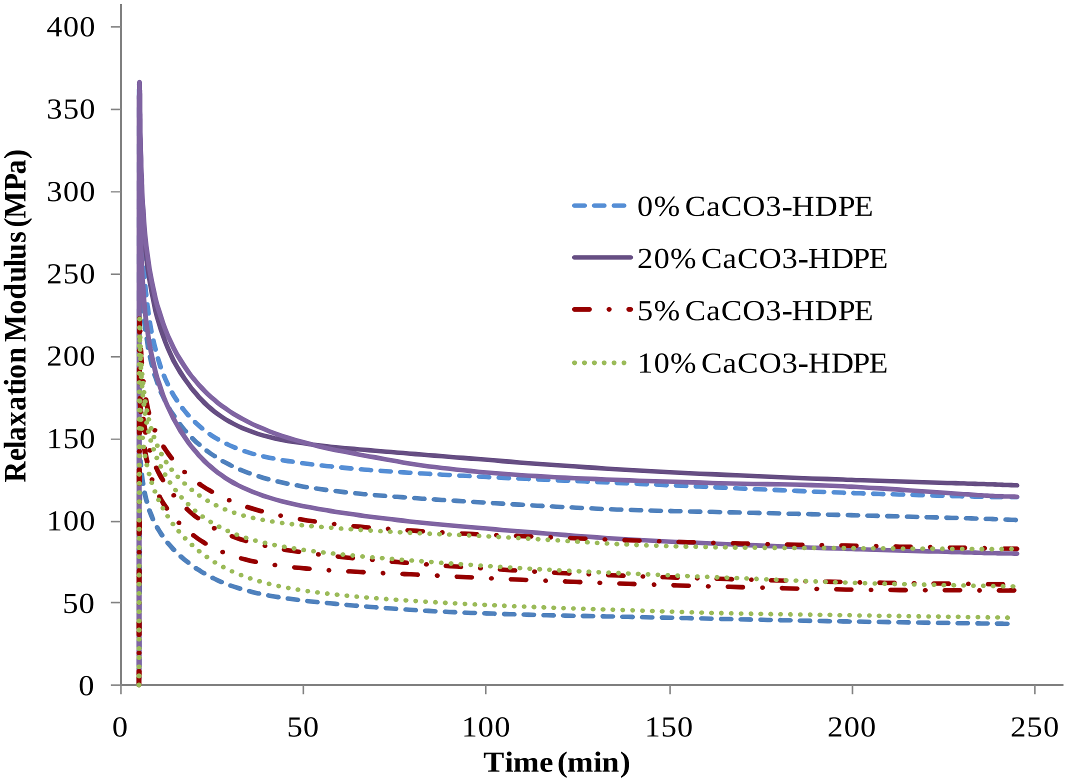

Figure 34: Plot of individual relaxation modulus vs. time for different HDPE-$CaCO_3$ composites

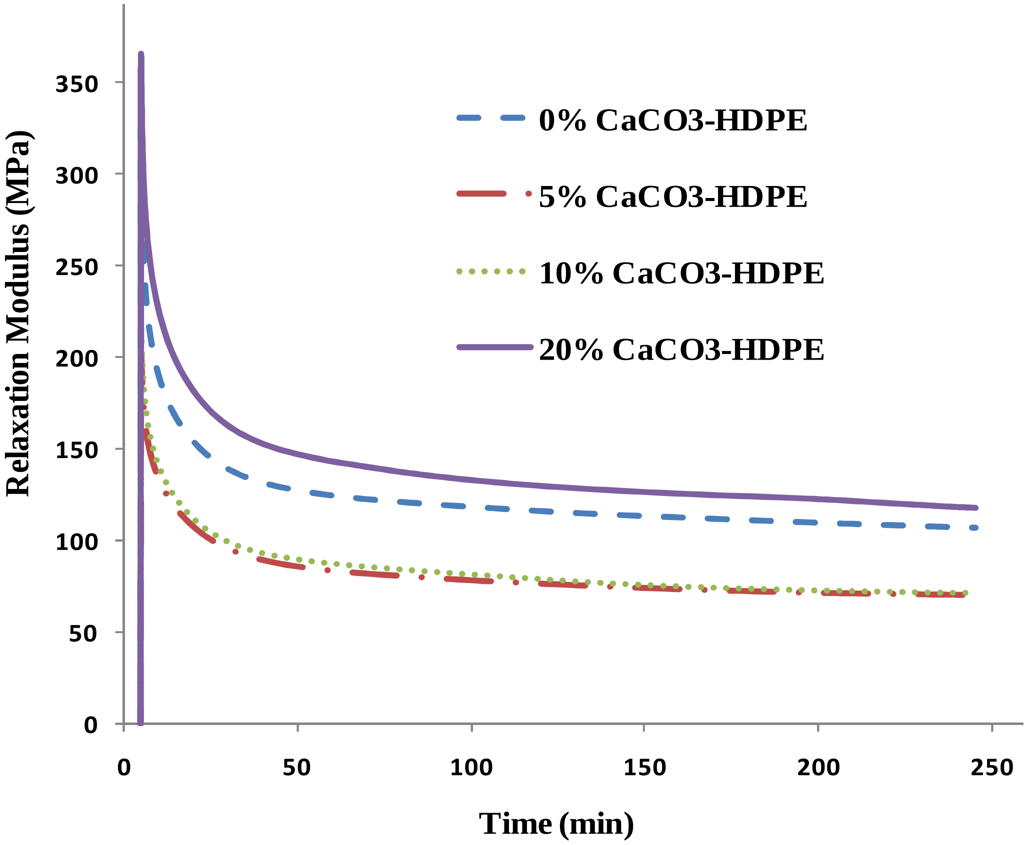

Figure 35: Plot of average relaxation modulus vs. time curve for HDPE- $CaCO_3$ composites

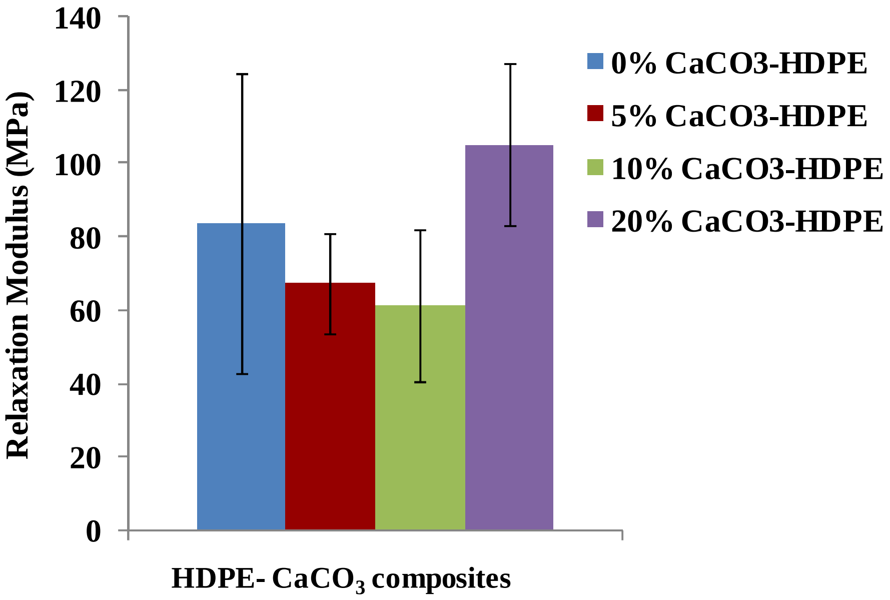

Figure 36: Average relaxation modulus for HDPE- $CaCO_3$ composites after 240 min.

From the stress relaxation curves, it was observed that incorporation of $CaCO_3$ in HDPE by 20% weight fraction increases the relaxation modulus. After 240 min, the average relaxation modulus for 20% $CaCO_3$-HDPE was found 25%[8] higher than the relaxation modulus of 0% $CaCO_3$-HDPE. However, addition of 5% and 10% $CaCO_3$, in fact lowered the relaxation modulus of the control HDPE. After 240 min of stress relaxation tests, average relaxation modulus for 5% $CaCO_3$ was found 20%[9] lower than that of the control HDPE, while for 10% $CaCO_3$ it was 27%[10] lower than the control HDPE.

---

[8] ((105 MPa-84 MPa)/84 MPa)×100
[9] ((67 MPa-84 MPa)/ 84 MPa)×100
[10] ((61MPa-84 MPa)/84 MPa)×100

4.2. Neat HDPE from Closure

For neat HDPE samples collected from caps, the effect of ageing and annealing were investigated. Stress relaxation was set as a parameter for determining ageing and annealing effects.

4.2.1 Ageing

The ageing effect on neat HDPE was investigated for both non-annealed and annealed samples.

4.2.1.1 Non-annealed samples

Figure 37 shows the stress relaxation curves for non-annealed samples. The samples were collected just after the injection molding machine and were tested after increasing lengths of time about 15 to 30 min each as indicated. 15 samples were tested from the non-annealed batch. Figure 39 shows the stress at different test times for samples aged at different times.

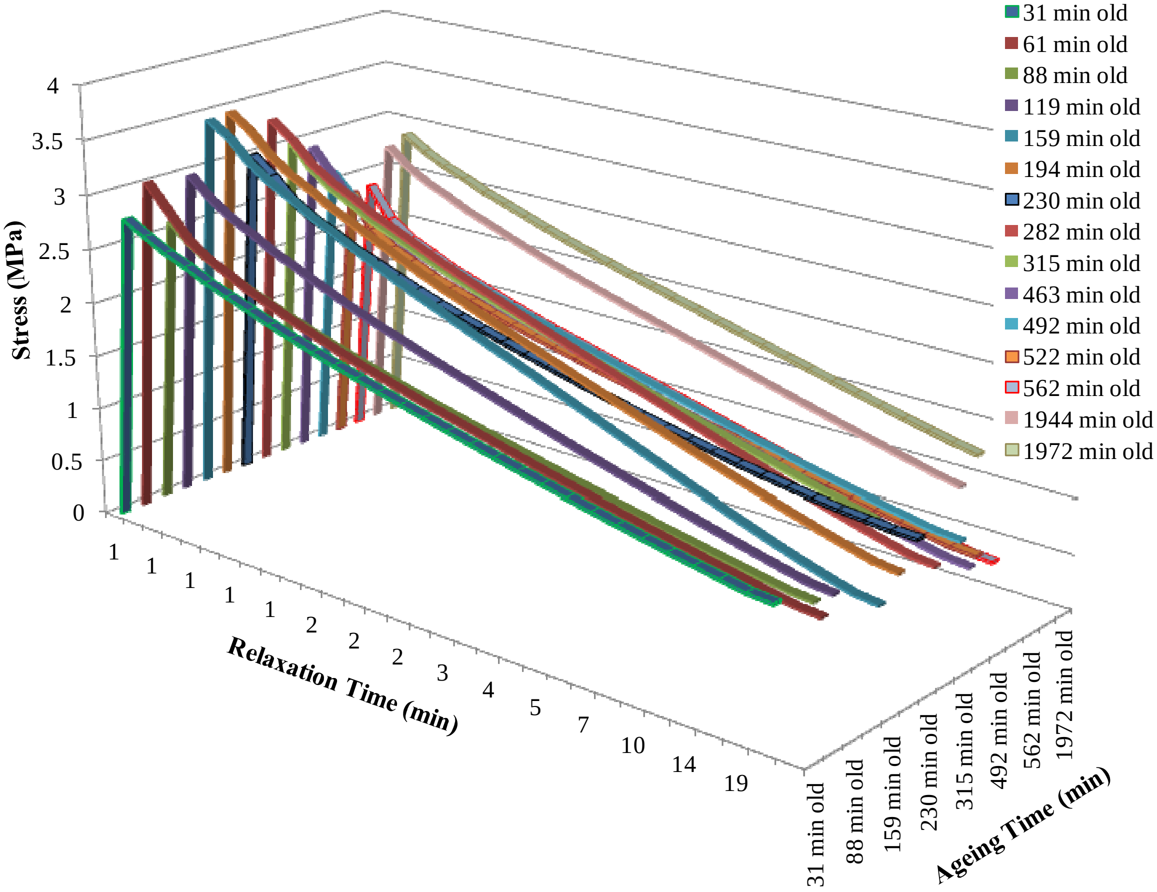

Figure 37: Plot of relaxed stress in non annealed sample having increased age (3D).

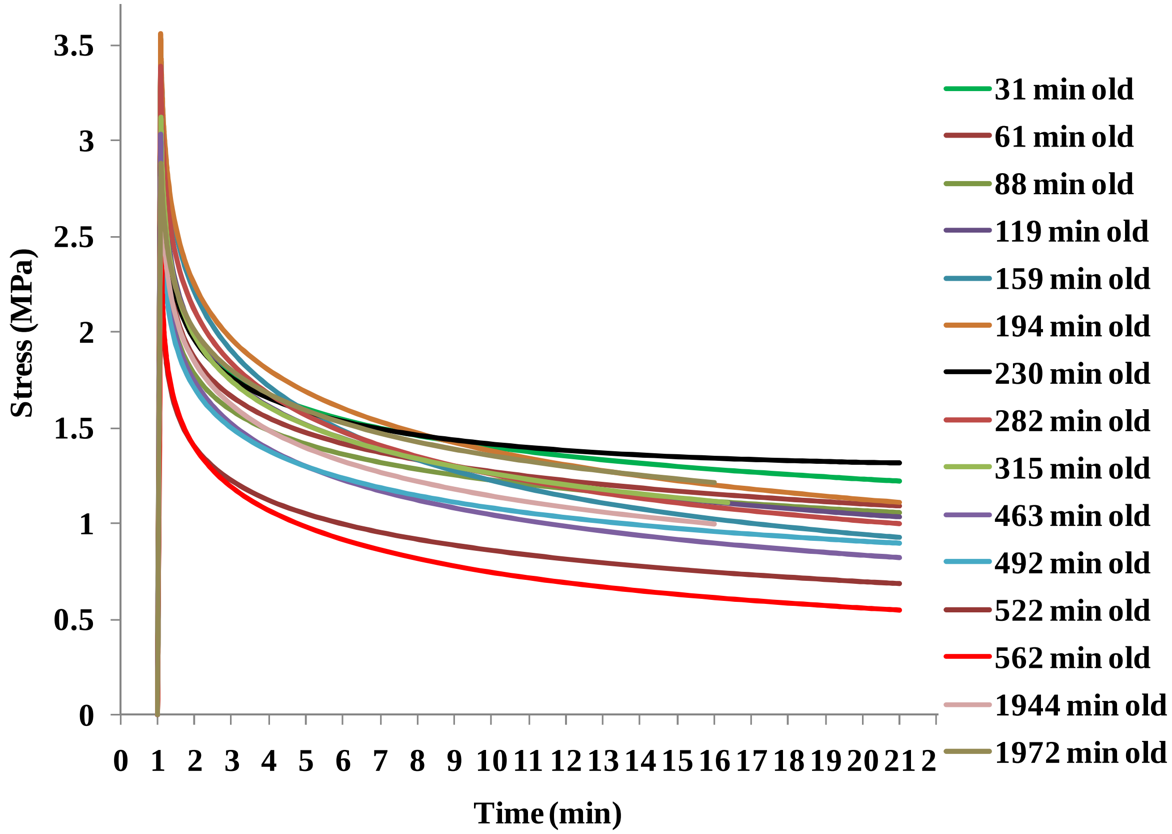

Figure 38: Plot of relaxed stress in non annealed sample having increased age (2D).

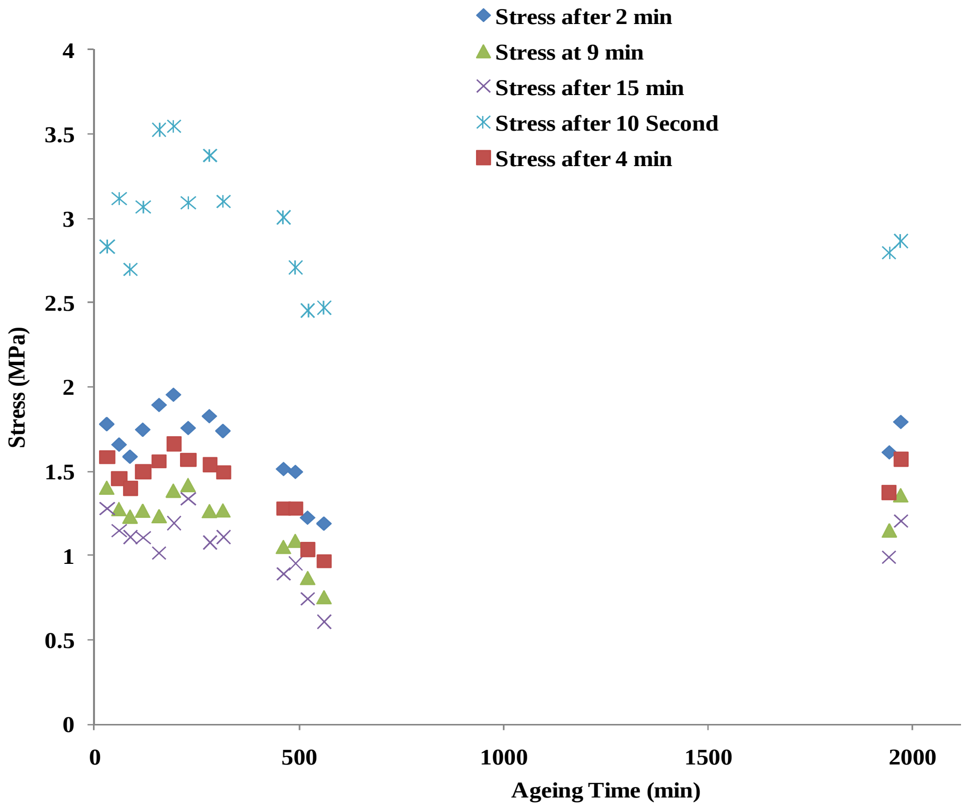

Figure 39: Stress vs. ageing time at different test time (Non-annealed sample).

Figure 38 shows a wide range of relaxed stresses for the non-annealed samples. No definite relationship was observed between the ageing time and the relaxed stress. Figure 39 shows the stress at different test times for the samples aged at different times. More experiments should be conducted in the big gap of data points of Figure 39. The reason for getting a wide range of stress relaxation curves can be explained by the concept of molecular equilibrium. Samples were collected from injection molded caps. In the injection molding process caps undergo rapid cooling and so some residual stress could be trapped, so molecules of the polymers were not at equilibrium. Therefore, for non-annealed samples, polymeric molecules were running toward equilibrium with time and, as a result, a wide variety of stress relaxation behavior was observed.

4.2.1.2 Annealed samples

Annealed for 30 minutes

Figure 40 and Figure 41 show the stress relaxation curves for 30 minute annealed samples. Figure 42 depicts the relaxed stress as a function of ageing time at different test time of stress relaxation tests. 7 samples were tested at different times after the samples were taken out of the oven.

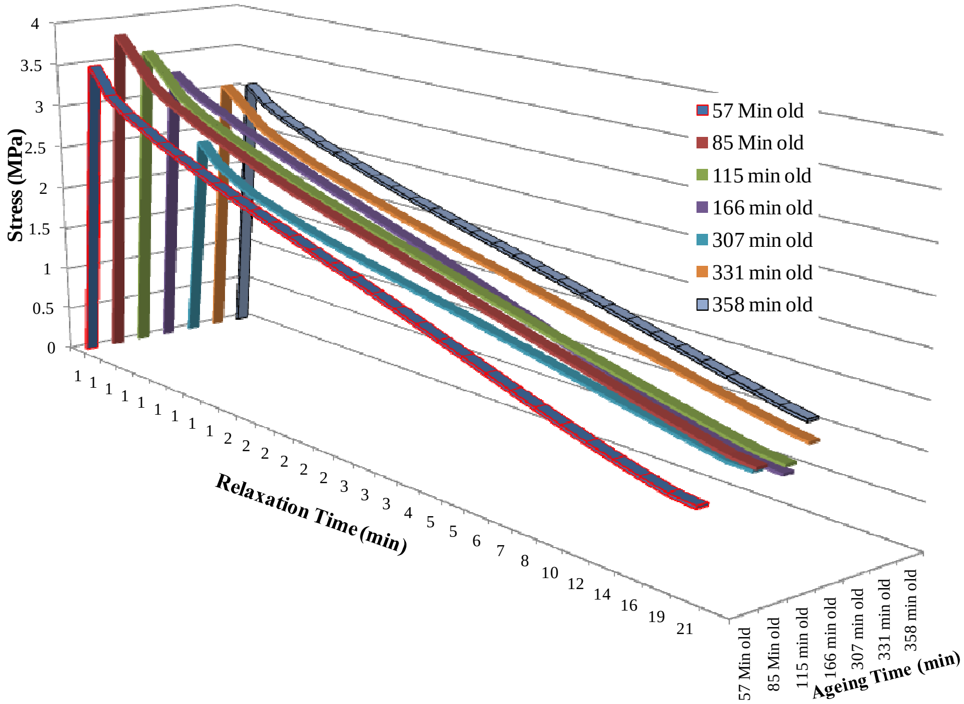

Figure 40: Plot of relaxed stress in annealed (30min) sample having increased age (3D).

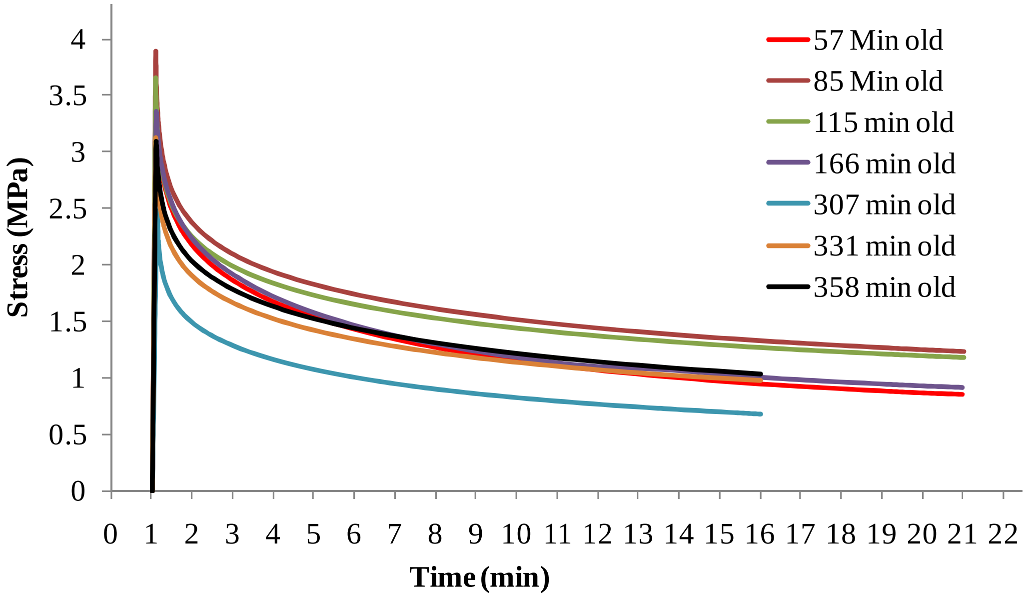

Figure 41: Plot of relaxed stress in annealed (30 min) samples having increased age (2D).

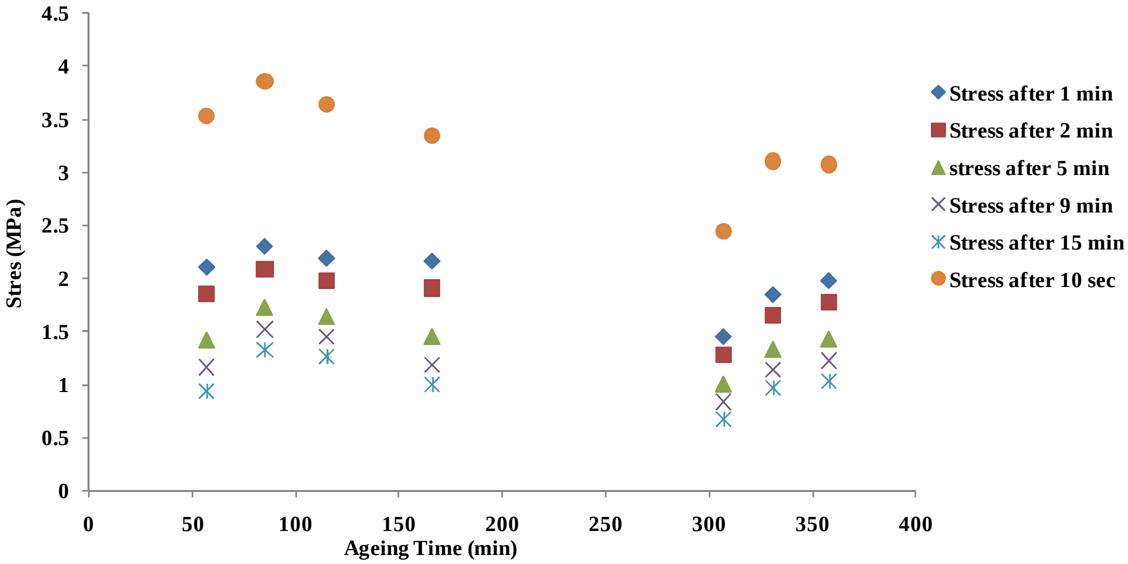

Figure 42: Stress vs. ageing time at different test time. Samples were annealed at 125°C for 30 minutes.

Annealed for 1 hour

Figure 43 and Figure 44 show the effect of ageing on 1 hour annealed samples. Figure 45 shows effect of ageing time on stresses at different test time.

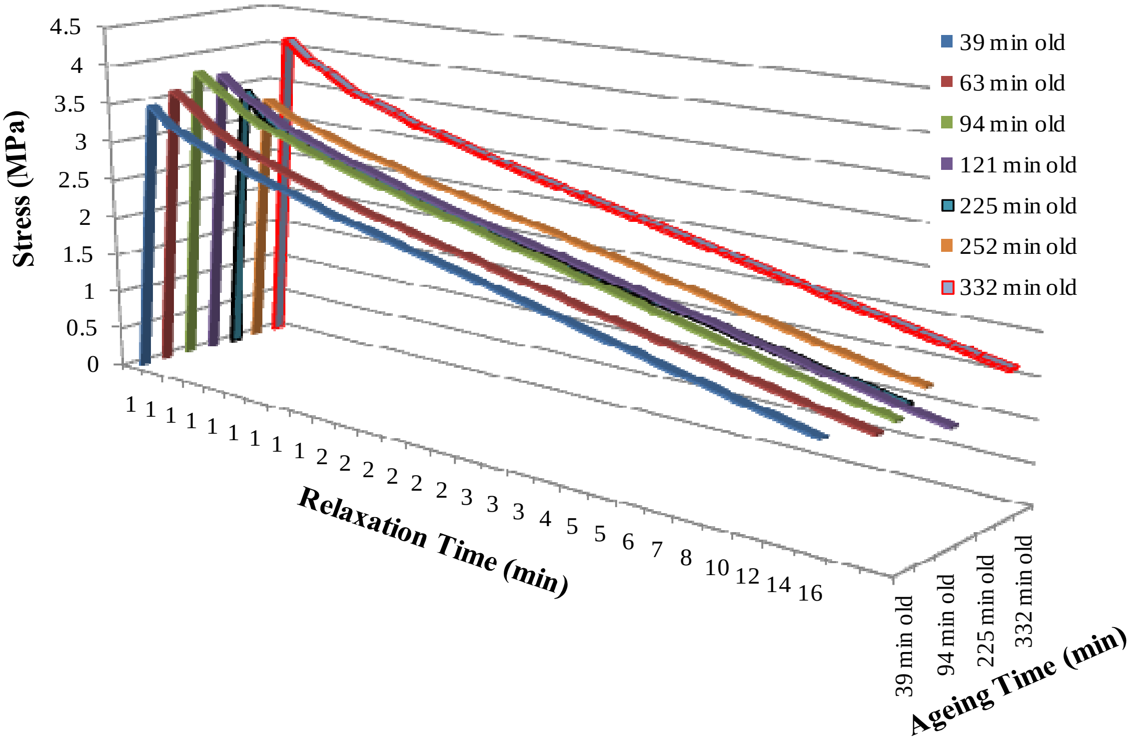

Figure 43: Plot of relaxed stress in annealed (1 hour) sample having increased age (3D)

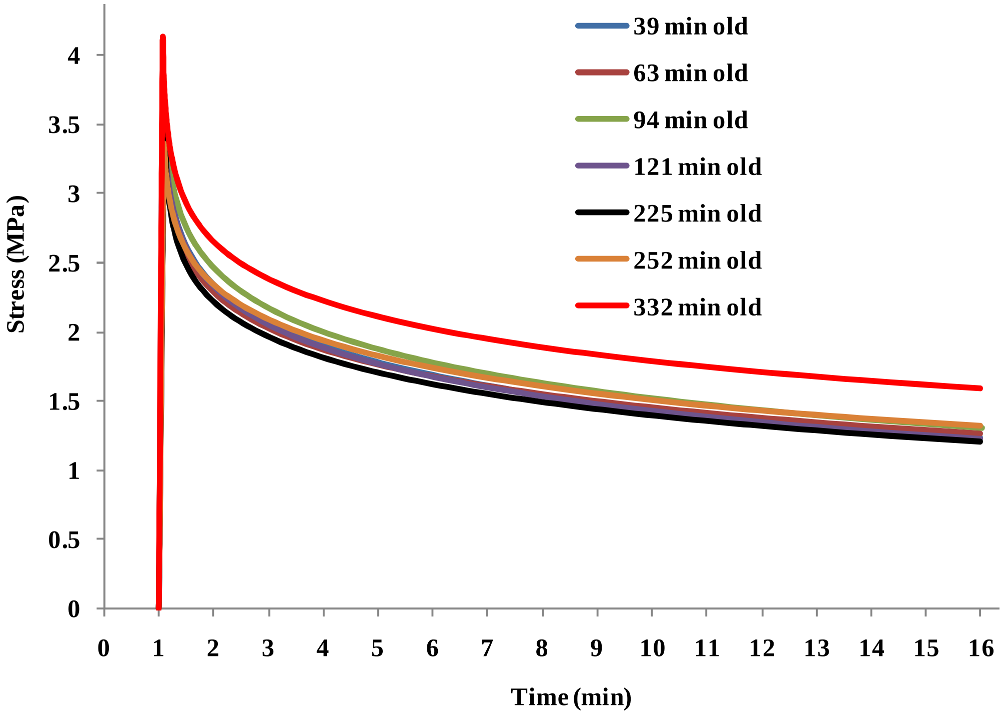

Figure 44: Plot of relaxed stress in annealed (1 hour) sample having increased age (2D)

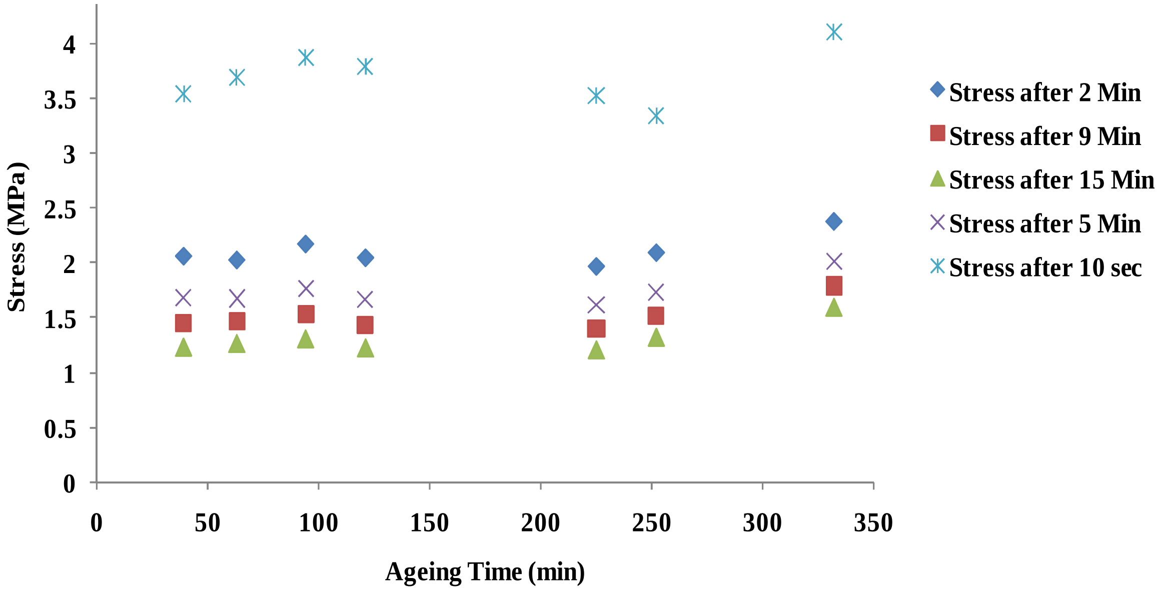

Figure 45: Stress vs. ageing time at different test time. Samples were annealed at 125^{o}C for 1 hour.

Unlike non-annealed and 30 minutes annealed samples, the stress relaxation curves for 1 hour annealed samples are not widely distributed. The reason of this kind of behavior is annealing accelerates ageing. Annealing at 1 hour provides sufficient time and energy to remove residual stress and the molecules of the polymer settle in more equilibrium states than the non-annealed and 30 minute annealed samples. Therefore, ageing after 1 hour annealing did not show any significant effect on the stress relaxation of the samples. On the other hand, the samples which were annealed for 30 minutes had less time and energy to reach in equilibrium, than the samples which were annealed for 1 hour. As a result, they were not completely in equilibrium and still some residual stress could exist. So, further ageing after annealing showed effects on the stress relaxation tests of these samples. The samples which were not annealed at all, showed a much wider range of stress relaxation curves as their molecules were not in equilibrium. With time, their molecules were moving towards equilibrium. Figure 46 shows the standard deviation of different samples as a function of annealing time after 15 min of stress relaxation tests. Standard deviation of average stress was found 32%[11] less for 1 hour annealed HDPE than the non-annealed HDPE.

---

[11] $((0.195-0.131)/0.195)\times 100$

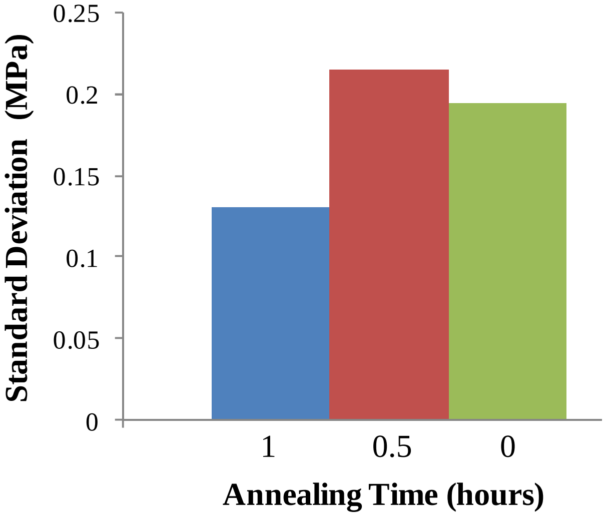

Figure 46: Standard deviation of stress among different samples as a function of annealing time after 15 min of stress relaxation tests

4.2.2. Annealing

Figure 47 shows the stress relaxation curves for annealed and non-annealed samples. From the figure, the relaxation modulus for 1 hour annealed HDPE is significantly higher than that of non-annealed, and 30 minute annealed HDPE. Figure 48 depicts the comparison of average stresses at different time of stress relaxation tests for annealed and non-annealed HDPE. HDPE annealed for 1 hour showed higher stress than the other two shorter times throughout the entire stress relaxation test. After 15 minutes of stress relaxation, HDPE annealed for 1 hour held 24% higher average stress than the non-annealed HDPE. At the beginning of the relaxation tests, 30 minute annealed samples showed slightly higher values of stresses than the non-annealed samples. But as tests went on, stresses for 30 minute samples were found lower than non-annealed samples (Figure 48).

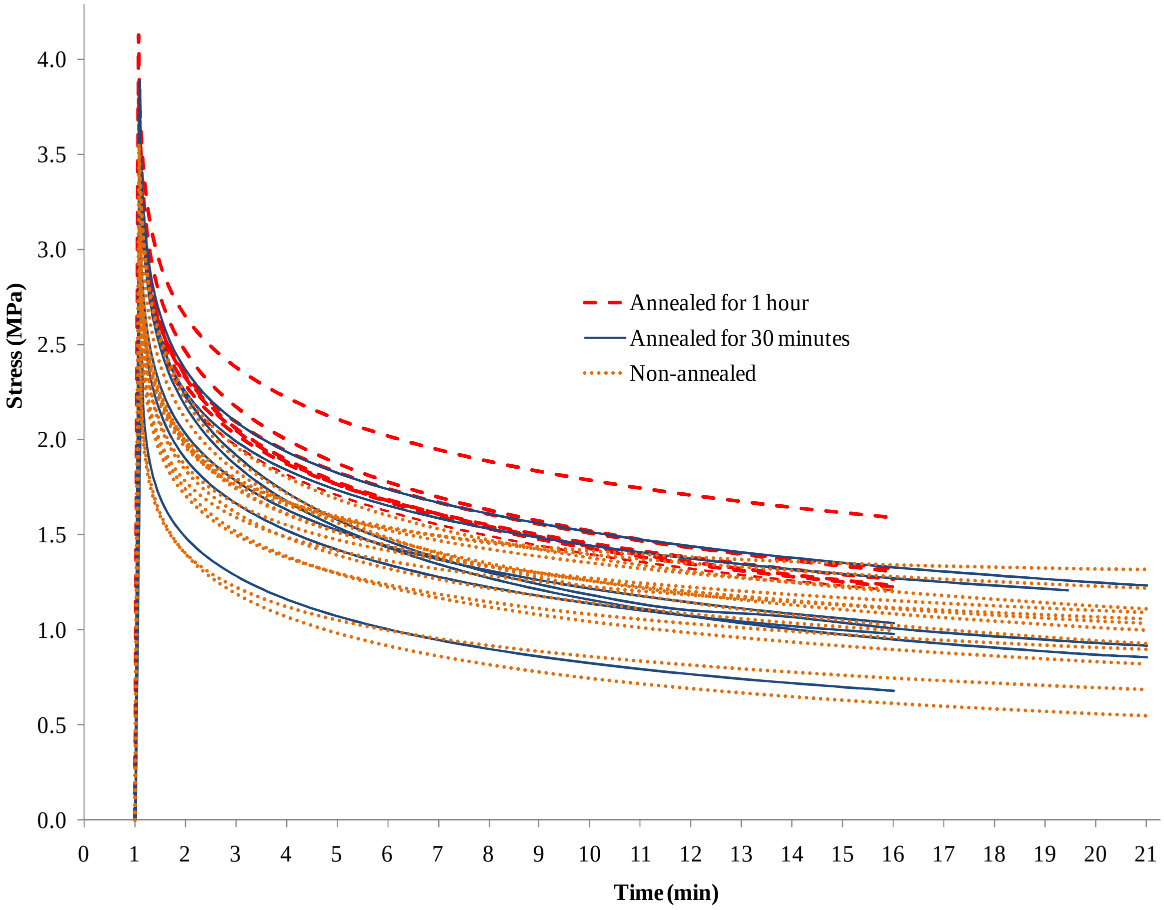

Figure 47: Plot of stress relaxation curves for annealed and non annealed HDPE

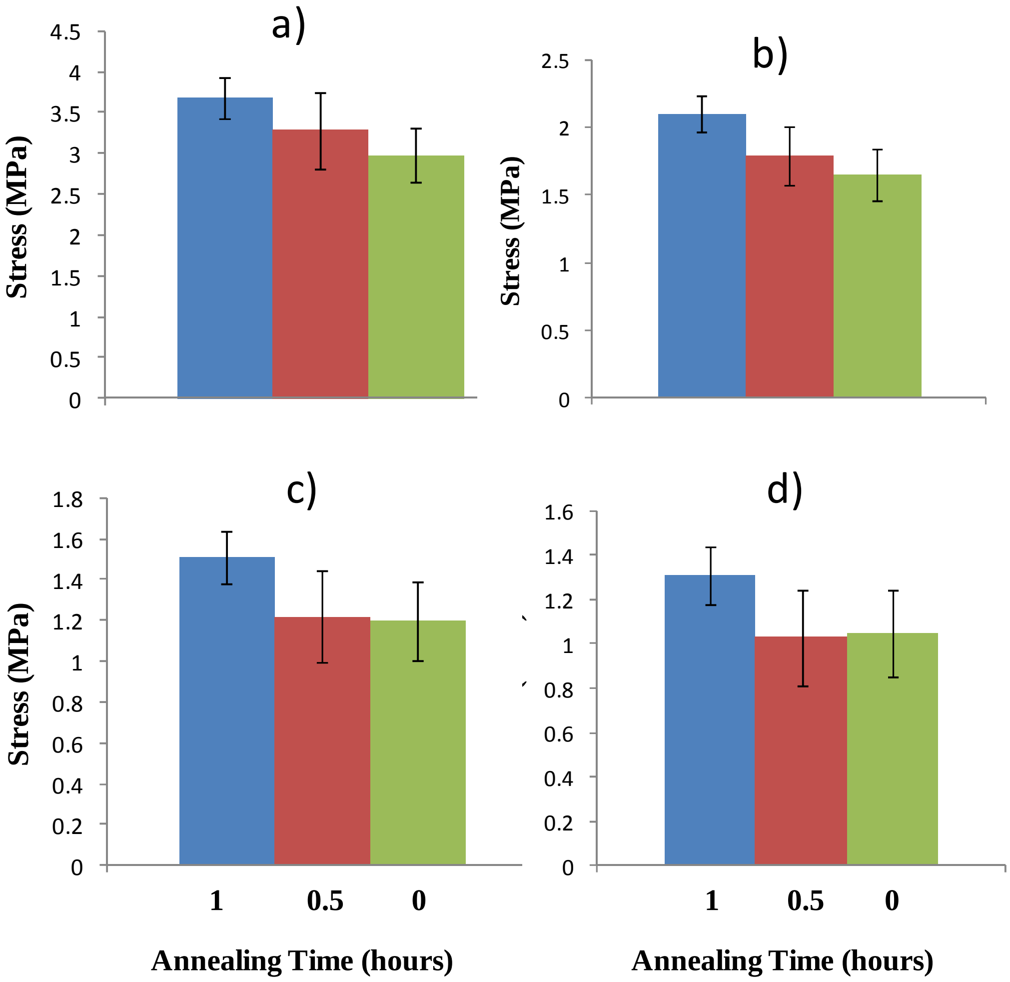

Figure 48: Comparison of stresses for non-annealed and annealed samples at 4 test times of stress relaxation tests; a) after 10 seconds, b) after 2 minutes, c) after 9 minutes, d) after 15 minutes.

From Figure 47 and Figure 48 it is evident that 1 hour annealing increases the stress for relaxation of neat HDPE. This is speculated that for 1 hour annealing, residual stresses were removed as molecules had enough time to reach equilibrium. As annealing can also increase the crystallinity of HDPE [99], this could be another reason for the increase in relaxation modulus.

For high speed manufacturing this one factor may be the most important one uncovered in the present work. Ageing reduces variation through eliminating residual stresses. Reduced variation is important when manufacturing on high speed lines. Less variation means less jam or other inconsistencies during the automated handling and application of caps. Along with consistent leak pressures, the generally increased stress relaxation should lead to increased seal strength for HDPE used as caps.

4.3. Seal Failure from Squeeze Pressure

The importance of seal failure in industry and its relevance with materials properties provoked us to study the closure seal failure from pressure across different finishes available in market. Figure 49 shows the comparison of seal failure load among different closures and finishes. This figure also shows the relative performance. Figure 50 depicts the load required for 5mm side wall deformation during the seal failure experiments. The side wall stiffness of different bottles were determined until 10 mm side wall displacement during the seal failure experiments, and are shown in Figure 51.

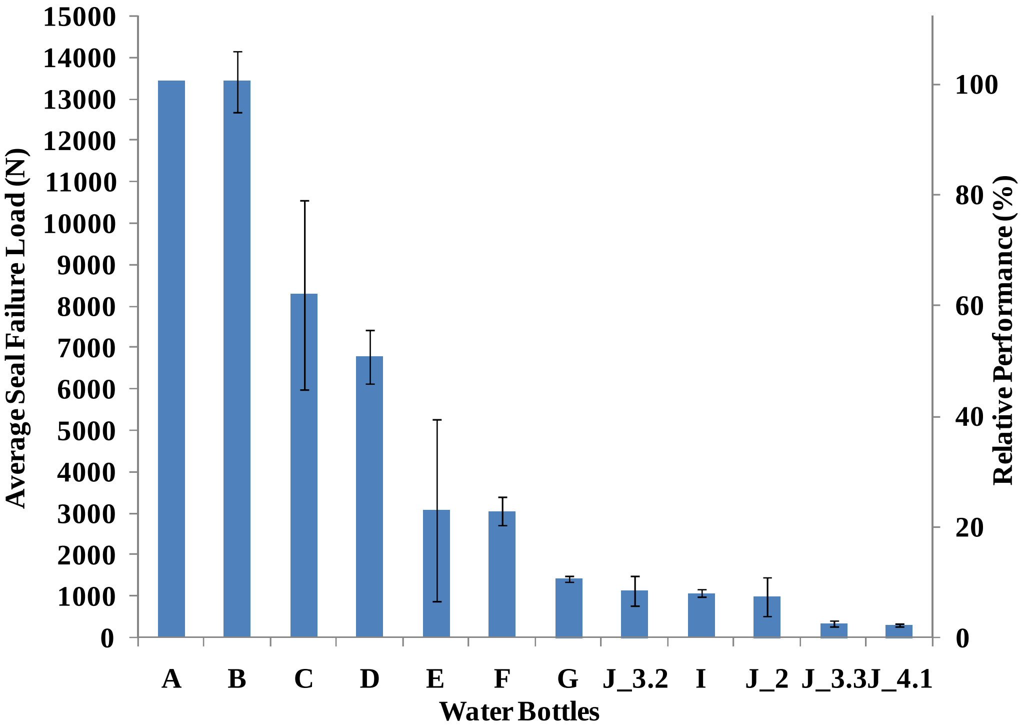

Figure 49: Comparison of seal failure load among different bottle designs

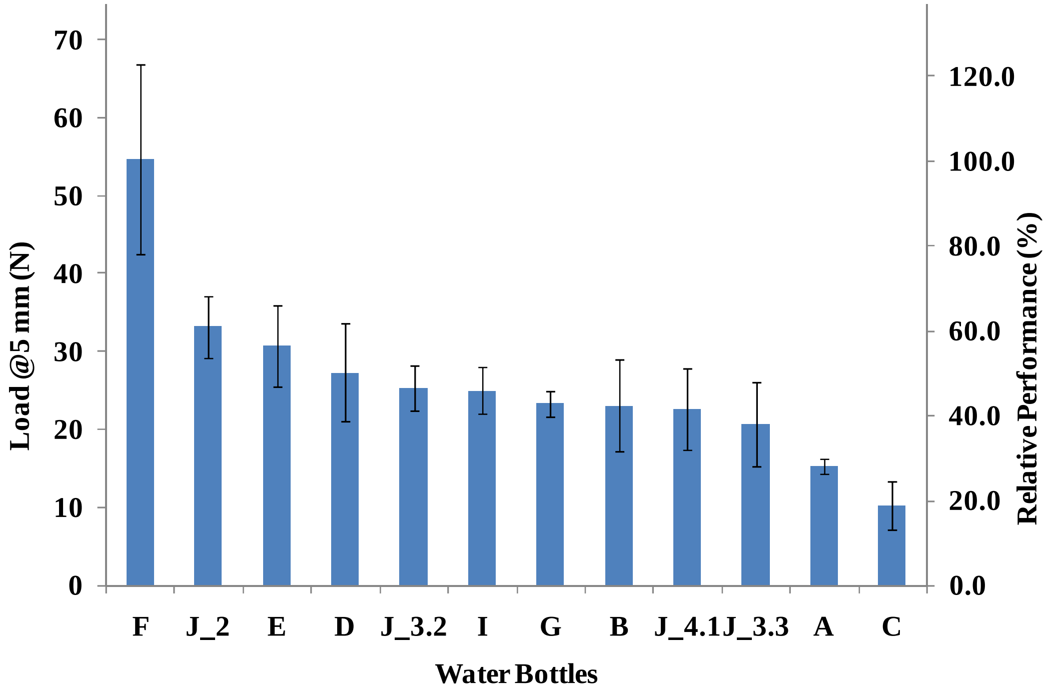

Figure 50: Comparison of Loads required for 5 mm side wall deformation among different bottle designs

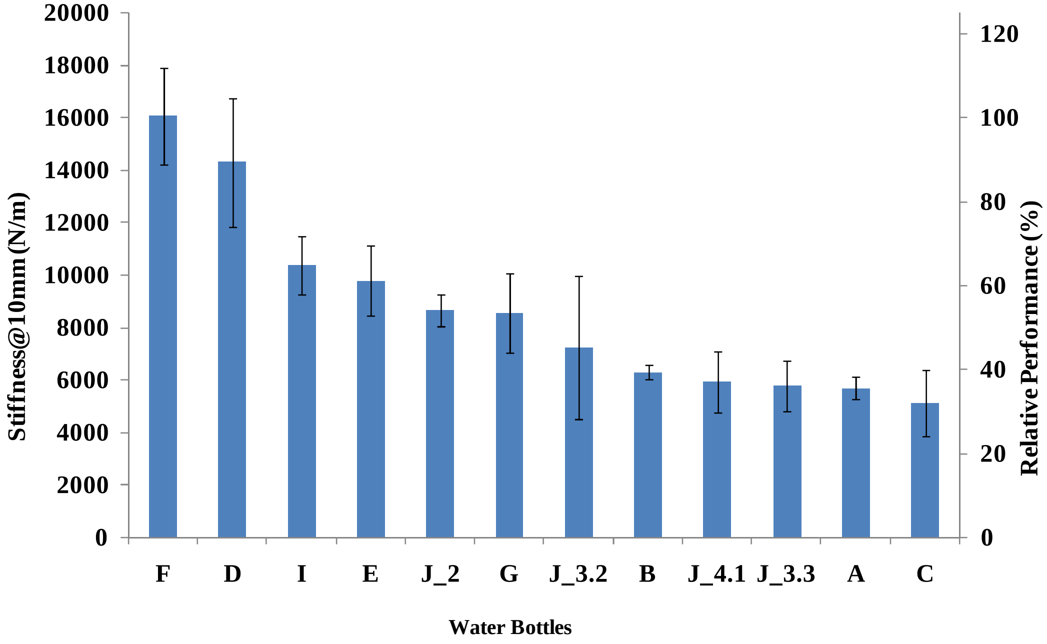

Figure 51: Comparison of side wall stiffness among different bottle designs

Figure 49 shows a wide range of seal failure loads, among different bottle designs. This wide range of failure loads depicts over-engineered products existed in the market. Proper designing and understanding of material properties can facilitate reducing polymer usage in the bottle industry, and hence make it beneficial on both environmental and economical fronts. Proper designing involves optimization of several factors such as seal failure load, stiffness of the bottles, and material consumption in manufacturing. Observation from Figure 49, Figure 50, and Figure 51 showed that less stiff bottles can posses higher seal failure loads.

This work shows for HDPE, creep strain can be reduced and relaxation modulus can be increased by incorporating $CaCO_3$. This work also reveals relaxation modulus can be increased by annealing heat treatment. Both creep strain and relaxation moduli are related to the final performance of the HDPE product. So these approaches have potential to increase the seal leak load of closures made with HDPE without increasing polymer usage.

CHAPTER V

5. Conclusions

Viscoelastic properties, creep behavior, and stress relaxation of HDPE were investigated, and improved by incorporation of $CaCO_3$ filler content and annealing heat treatment.

- At 30^o C, the storage modulus increased around 23%[12] for 20% $CaCO_3$ HDPE composite over the control HDPE. The loss modulus was also observed to increase at higher weight fraction of $CaCO_3$ in HDPE, when tested as a function of temperature.
- No significant change of storage and loss modulus was observed by increasing $CaCO_3$ weight fraction from 5% to 10%.
- The addition of $CaCO_3$ did not show significant change in tan delta at different temperatures. This observation concurs with the results of Yang *et al.*[59]
- After 12 hours, the average creep strain for the 20% $CaCO_3$-HDPE composite was found 30%[13] lower than the average creep strain of the control HDPE. Creep

---

[12] $((1395\text{-}1135^oC)/1135\,C \times 100)$

[13] ((5.25-3.65)/5.25)*100

strain did not change significantly as $CaCO_3$ content was increased from 5% to 10%.

- The relaxation modulus of HDPE was increased by 25%[8] in 20% $CaCO_3$-HDPE over the control HDPE. However, 5% and 10% $CaCO_3$-HDPE composites showed a lower relaxation modulus in stress relaxation tests than the 0% $CaCO_3$-HDPE.
- Ageing did not show any regular pattern or trend on the relaxation modulus of HDPE.
- Annealing for 1 hour showed less variation of stress relaxation among different samples than the non-annealed HDPE. The standard deviation of average stress was found 32% less for 1 hour annealed HDPE than non-annealed HDPE after 15 minutes of stress relaxation.
- After 15 minutes of stress relaxation, HDPE annealed at 125°C for 1 hour, held 24% higher average stress than the non-annealed HDPE.

.

CHAPTER VI

6. Future Work

- Increasing the weight fraction of $CaCO_3$ more than 20% and analyzing the corresponding properties changes for an optimal weight fraction could extend this work
- Dispersion of $CaCO_3$ in the composites can be related to the observed performance and can be studied through SEM and TEM analysis.
- Response of the materials by a large range of static stress and strain in the creep, and stress relaxation tests aids learning.
- Other filler materials like Glass Fiber can be tested in HDPE instead of $CaCO_3$ for comparison.
- Annealing should be done at several other temperatures and time periods for better prediction and optimization.

REFERENCES

---

[1] J. A. Brydson, *Plastic Materials,* 4th ed. Mansell Ltd., Witham, Essex, 1982

[2] J. J. Cheng, "Mechanical and Chemical Properties of High Density Polyethylene: Effects of Microstructure on Creep Characteristics," Ph.D. dissertation, Chemical Engineering, University of Waterloo, Waterloo, 2008.

[3] I. M. Ward, “Mechanical Properties of Solid Polymers”, Toronto: Wiley-Interscience, 1971.

[4] A. Keller, "A note on single crystals in polymers: Evidence for a folded chain configuration," *Philosophical Magazine,* vol. 2, pp. 1171 - 1175, 1957.

[5] O. g. Piringer and A. L. Baner, “Characteristics of Plastic Materials” in *Plastic Packaging: Interactions with Food and Pharmaceuticals,* 2nd ed. Germany: Wiley-VCH, 2008, pp. 32.

[6] V. R. Gowariker, N. V. Viswanathan and J. Sreedhar, “Individual Polymers” in *Polymer Science,* 1st Ed. Reprint, New Delhi, India: New Age International (P) Ltd., 2005, pp 217.

---

[7] S. Hosoda, *et al.*, "Degree of branch inclusion into the lamellar crystal for various ethylene/[alpha]-olefin copolymers," *Polymer,* vol. 31, pp. 1999-2005, 1990.

[8] L. H. Gabrlel, *Chapter 1: History and Physical Chemistry of HDPE,* [Online]. Available: http://www.plasticpipe.org/pdf/chapter-_history_physical_chemistry_hdpe.pdf

[9] H. A. Wittcoff, B. G. Reuben, J. S. Plotkin, “Chemicals and Polymers From Ethylene”, *Industrial Organic Chemicals,* 2nd ed. New Jersey: John Wiley & Sons Inc, 2004, pp 107.

[10] C. Vasile and M. Pascu, “Basic Types”, *Practical Guide to Polyethylene,* Shrewsbury, UK: Rapra Technology Ltd. , 2005, pp 17.

[11] A. A. Klyosov, “Composition of Wood-Plastic Composite Deck Boards Thermoplastics”, in *Wood-Plastic Composites,* New Jersey: John Wiley & Sons, Inc., 2007, pp 55.

[12] Cerena Research, 2011, “Introduction”, *Market Study: Polyethylene-HDPE,* [Online]. Available: http://www.ceresana.com/en/market-studies/plastics/polyethylene-hdpe/

[13] G. M. Swallowe, “Viscoelasticity”, in *Mechanical Properties and Testing of Polymers: An A-Z Reference,* G. M. Swallowe, ED., Dordrecht, The Netherlands: Kluwer Academic Publishers, 1999, pp 265-268.

[14] O. U. Colak and N. Dusunceli, "Modeling Viscoelastic and Viscoplastic Behavior of High Density Polyethylene (HDPE)," *Journal of Engineering Materials and Technology,* vol. 128, pp. 572-578, 2006.

[15] H. P. Menard, “An Introduction to Dynamic Mechanical Analysis”, in *Dynamic Mechanical Analysis: A Practical Introduction,*2nd ed., Boca Raton, Florida:CRC Press, 2008, pp 3-10.

[16] M. A. Meyers, K. K. Chawla, *Mechanical Behavior of Materials,* Prentice Hall, 1999

[17] L. E. Nielsen, “Creep and Stress Relaxation”, in *Mechanical Properties of Polymers and Composites,* Vol.1, New York: Marcel Dekker, INC., 1974 pp 65-77.

[18] S.I. Farag, *et al.*, “Application of Sorption-Desorption Moisture Transfer Modeling to the Study of Chemical Stability of a Moisture-Sensitive Drug Product in Different Packaging Configurations,” *Int. J. Pharm.,* vol. 223, pp. 1-13, 2001.

[19] J. Malik, *et al.*, “Processing Stabilization of HDPE: A Complex Study of an Additive Package,” *Polym. Degrad. Stab.*, vol. 50, pp. 329-336, 1995.

[20] P. Zygoura, *et al.*, “Shelf Life of Whole Pasteurized Milk in Greece: Effect of Packaging Material,” *Food Chem.*, vol. 87, pp 1-9, 2004.

[21] A. E. Akinay, *et al.*, "Prediction of long-term service performance of polymeric materials from short-term tests: Creep and prediction of the stress shift factor of a longitudinal polymer liquid crystal," *Polymer Engineering & Science,* vol. 41, pp. 977-981, 2001.

[22] J.G.J. Beijer & J.L. Spoormaker, “Solution strategies for FEM analysis with nonlinear viscoelastic polymers,” *Computers & Structures*, vol. 80, pp. 1213–1229, 2002

[23] A. Hernández-Jiménez, *et al.*, "Relaxation modulus in PMMA and PTFE fitting by fractional Maxwell model," *Polymer Testing*, vol. 21, pp. 325-331, 2002.

---

[24] R. Elleuch and W. Taktak, "Viscoelastic behavior of HDPE polymer using tensile and compressive loading," *Journal of Materials Engineering and Performance*, vol. 15, pp. 111-116, 2006

[25] H. Nakayasu, H. Markovitz and D. J. Plazek, “The Frequency and Temperature Dependndence of Dynamic Mechanical Properties of a High Density Polyehtylene,” *Journal of Rheology*, vol. 5, pp. 261-283, 1961.

[26] W.N. Findley, J.S Lai, & K. Onaram, *Creep and relaxation of nonlinear viscoelastic materials: With an Introduction to Linear Viscoelasticity*, Newyork: Dover Publications, Inc., 1989.

[27] C. Zhang and I. D. Moore, "Nonlinear mechanical response of high density polyethylene. Part I: Experimental investigation and model evaluation," *Polymer Engineering & Science*, vol. 37, pp. 404-413, 1997.

[28] R. Elleuch and W. Taktak, “Prediction of Compressive Creep and Relaxation of HDPE,” *International Journal of Modelling and Simulation*, vol. 26, pp. 4424-4429, 2006.

[29] O. U. Colak and N. Dusunceli, "Modeling Viscoelastic and Viscoplastic Behavior of High Density Polyethylene (HDPE)," *Journal of Engineering Materials and Technology*, vol. 128, pp. 572-578, 2006.

[30] J. F. Mano, *et al.* , “Viscoelastic behavior and time-temperature correspondence of HDPE with varying levels of process-induced orientation,” Polymer, vol. 42, pp. 6187-6198, 2001.

[31] V. Stefanovski, *et al.,”* Pipes From Recycled High Density Polyethylene Blends” in *ANTEC 2002 Plastics: Annual Technical Conference,* Vol. 3: Special Areas, ed: Society of Plastics Engineers, 2002

[32] S. Herzberg, L. Hornberger, “Effect of various processing stages on the Crystallinity of Post-Consumer Recycled HDPE” in *Antech’98,* Atlanta, Georgia, 1998, pp. 2935-2941.

[33] K. Khait, *et al.* , “Recovery of Post-Consumer Plastic Waste via Solid State Mechanochemistry”, in *Antech’2001,* ed.: SPE,2001. Pp. 2763-2766.

[34] S. N. Bhattacharya, *et al.*, “Introduction,” in *Nanocomposite: Theory and Practice*, Munich, Germany: Hannser, 2007, pp. 1-4.

[35] H. X. Nguyen and H. Ishida, "POLY(ARYL-ETHER-ETHER-KETONE) AND ITS ADVANCED COMPOSITES - A REVIEW," *Polymer Composites*, vol. 8, pp. 57-73, Apr 1987.

[36] H. Menendez and J. L. White, "A Wide-angle X-ray diffraction method of determining chopped fiber orientation in composites with application to extrusion through dies," *Polymer Engineering & Science*, vol. 24, pp. 1051-1055, 1984

[37] S. S. Roy, M. Okamoto, “Polymer/layered silicate nanocomposites: a review from preparation to processing” in *Prog. Polym. Sci.*, vol. 28, pp. 1539-1641, 2003.

[38] Y. Wang*, et al.*, "Crystallization and mechanical properties of T-ZnOw/HDPE composites," *Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing*, vol. 501, pp. 220-228, Feb 2009.

[39] R. N. Rothon, *Particulate-Filled Polymer Composites,* Harlow: Longman Scientific and Technical, 1995

[40] R. Rothon, "Mineral Fillers in Thermoplastics: Filler Manufacture and Characterisation," in *Mineral Fillers in Thermoplastics I*. vol. 139, J. Jancar, *et al.*, Eds., ed: Springer Berlin / Heidelberg, 1999, pp. 67-107.

[41] M. Hankook, *Particulate-Filled Polymer Composites,* R. Rothan, Ed., Essex, UK: Longman Scientific & Technical, 1995.

[42] Z. Bartczak, et al., “Toughness mechanism in semi-crystalline polymer b1ends:II. High-density polyethylene toughened with calcium carbonate filler particles” in *polymer*, vol. 40, pp. 2347-2365, 1999.

[43] S. Wu, *et al.*, "Rigid Toughening **Of** Polyolefin with Calcium Carbonate Particles," in *Antec,* Proceedings: SPE, 2002.

[44] S. Sahebian, *et al.*, "The effect of nano-sized calcium carbonate on thermodynamic parameters of HDPE," *Journal of Materials Processing Technology,* vol. 209, pp. 1310-1317, 2009.

[45] S. M. Zebarjad, *et al.*, “"A *study on thermal behaviour* ***of*** *HDPE/CaC03 nanocomposites”,*in *Journal of Achievements in Materials and Manufacturing Engineering,* Vol. 17 (2), pp. 173-176, 2006.

[46] L. E. Nielson, *Mechanical Properties of Polymers and Composites*, NewYork: Marcel Deker Inc., 1974

[47] L. E. Nielsen, "Creep and Dynamic Mechanical Properties of Filled Polyethylenes," *Transactions of the Society of Rheology,* vol. 13, pp. 141-166, 1969.

[48] K. Kendall and F. R. Sherliker, "Colloidal Reinforcement: The Influence of Bound Polymer," *British Polymer Journal,* vol. 12, pp. 85-88, 1980.

[49] V. P. Chacko, *et al.*, "Morphology of CaCO3-filled polyethylenes," *Journal of Polymer Science: Polymer Physics Edition*, vol. 20, pp. 2177-2195, 1982.

[50] V. D. Svehlova, "Influence of adhesion between filler and matrix on mechanical properties of filled polyethylene", *Journal of Macromolecular Science, Part B: Physics*, vol. 21(2), pp. 231-242, 1982.

[51] F. H. J. Maurer, *et al.*, "Interfacial interaction in kaolin-filled polyethylene composites," *Colloid & Polymer Science*, vol. 263, pp. 624-630, 1985.

[52] J. Kubát and M. Rigdahl, "Activation volumes for flow processes in solids," *Materials Science and Engineering*, vol. 24, pp. 223-232, 1976.

[53] J. Kubat, "Stress Relaxation in Solids," *Nature*, vol. 205, pp. 378-379, 1965.

[54] C. G. Ek, *et al.*, "Stress relaxation, creep, and internal stresses in high density polyethylene filled with calcium carbonate," *Rheologica Acta*, vol. 26, pp. 55-63, 1987.

[55] T. B. Lewis and L. E. Nielsen, "Dynamic mechanical properties of particulate-filled composites," *Journal of Applied Polymer Science*, vol. 14, pp. 1449-1471, 1970.

[56] J. C. M. Li, "DISLOCATION DYNAMICS IN DEFORMATION AND RECOVERY," *Canadian Journal of Physics*, vol. 45, pp. 493-509, 1967.

[57] R. Kosfel, T. Uhlennbroich, FHJ. Maurer, *Proc. Intern Symp polymer Additives*, Las Vegas: Amer Chem. Soc, 1982, pp. 289.

[58] J. Kubát, *et al.*, "Internal stresses in polyethylene as related to its structure," *Materials Science and Engineering*, vol. 19, pp. 185-191, 1975.

[59] Y. L. Yang, *et al.*, "Dynamic Mechanical Properties and Morphology of High-Density Polyethylene/CaCO3 Blends With and Without an Impact Modifier," *Journal of Applied Polymer Science*, vol. 103, pp. 3907-3914, 2007.

---

[60] R. H. Elleithy, *et al.,* “High Density Polyethylene/Micro Calcium Carbonate Composite: A Study of Morphological, Thermal, and Viscoelastic Properties,” *Journal of Applied Polymer Science*, vol. 117, pp. 2413-2421, 2010.

[61] J. Grabowaska, *et al.,* “The Rheological and Mechanical Properties of Virgin HDPE/CaCO3 and Recycled HDPE/CaCO3 Blends,” *Antec*, 2010, pp. 1754.

[62] S. Sahebian, *et al.*, "The effect of nano-sized calcium carbonate on thermodynamic parameters of HDPE," *Journal of Materials Processing Technology,* vol. 209, pp. 1310-1317, Feb 2009.

[63] A. Lazzeri, *et al.*, "Filler toughening of plastics. Part 1 - The effect of surface interactions on physico-mechanical properties and rheological behaviour of ultrafine CaCO3/HDPE nanocomposites," *Polymer,* vol. 46, pp. 827-844, Jan 2005.

[64] X. Dai, *et al.*, "Preparation and properties of HDPE/CaCO3/OMMT ternary nanocomposite," *Polymer Engineering & Science,* vol. 50, pp. 894-899, 2010.

[65] J.-W. Huang, *et al.*, "Nonisothermal crystallization of high density polyethylene and nanoscale calcium carbonate composites," *Polymer Engineering & Science,* vol. 48, pp. 1268-1278, 2008.

[66] S. Sahebian, *et al.*, "Effect of both uncoated and coated calcium carbonate on fracture toughness of HDPE/CaCO3 nanocomposites," *Journal of Applied Polymer Science,* vol. 104, pp. 3688-3694, 2007

[67] P. R. Hornsby and K. Premphet, "Influence of phase microstructure on the mechanical properties of ternary phase polypropylene composites," *Journal of Applied Polymer Science,* vol. 70, pp. 587-597, 1998

[68] P. Hornsby, "Rheology, Compounding and Processing of Filled Thermoplastics," in *Mineral Fillers in Thermoplastics I.* vol. 139, J. Jancar, *et al.*, Eds., ed: Springer Berlin / Heidelberg, 1999, pp. 155-217.

[69] J. R. White, "Polymer ageing: physics, chemistry or engineering? Time to reflect," *Comptes Rendus Chimie,* vol. 9, pp. 1396-1408.

[70] A. V. Iacopi and J. R. White, "Residual stress, aging, and fatigue fracture in injection molded glassy polymers I. Polystyrene," *Journal of Applied Polymer Science,* vol. 33, pp. 577-606, 1987.

[71] L. C. E. Struik, *Physical aging in amorphous polymers and other materials / L. C. E. Struik*. Amsterdam ; New York : New York :: Elsevier Scientific Pub. Co. ; distributors for the U.S. and Canada, Elsevier North-Holland, 1978.

[72] A. Kovacs, "Transition vitreuse dans les polymères amorphes. Etude phénoménologique," in *Fortschritte Der Hochpolymeren-Forschung*. vol. 3, ed: Springer Berlin / Heidelberg, 1964, pp. 394-507.

[73] A.J. Kovacs*, et al., The Structure of Non-Crystalline Materials,* P. H. Gaskell, Ed., London: Tylor an Francis, pp. 153, 1977.

[74] A. J. Kovacs and J. M. Hutchinson, "Isobaric thermal behavior of glasses during uniform cooling and heating: Dependence of the characteristic temperatures on the relative contributions of temperature and structure to the rate of recovery. II. A one-parameter model approach," *Journal of Polymer Science: Polymer Physics Edition,* vol. 17, pp. 2031-2058, 1979.

---

[75] C. K. Chai and N. G. McCrum, "The freezing-in of non-equilibrium values of the limiting compliances as a mechanism of physical ageing," *Polymer,* vol. 25, pp. 291-298, 1984.

[76] N. G. McCrum, “Sequential Relaxation as the Mechanism of Physical Ageing in Amorphous Polymers”, *Polymer Communications*, vol. 25 (1), pp. 2-4, 1984.

[77] N. G. McCrum, “Interpretation of Physical Ageing in Creep and DMTA from Sequential Ageing Theory”, *Plastics, Rubber and Composites Processing and Applications*, vol. 18 (2), pp. 181-191, 1992.

[78] R. E. Robertson*, et al.*, "Free volume and the kinetics of aging of polymer glasses," *Macromolecules,* vol. 17, pp. 911-919, 1984.

[79] A. Siegmann and S. Kenig, "Simultaneous residual stresses and crystallinity changes during ageing of polyoxymethylene," *Journal of Materials Science Letters,* vol. 5, pp. 1213-1215, 1986.

[80] J. R. White, "Effect of secondary crystallization on residual stresses in moulded polymers," *Journal of Materials Science Letters,* vol. 9, pp. 100-101, 1990.

[81] N. G. McCrum, *Molecular Basis of Transitions and Relaxations,* D. J. Meier, Ed., London: Gordon and Breach, 1978, pp. 167.

[82] L. C. E. Struik, “Long Term Physical Ageing of Polypropylene at Room Temperature”, *Plastic and Rubber Processing and Applications,* vol. 2, pp. 41-50, 1982.

[83] L. C. E. Struik, “The mechanical and physical ageing of semicrystalline polymers: 1” *Polymer,* vol. 28, pp. 1521-1533. 1987.

[84] L. C. E. Struik, “The mechanical and physical ageing of semicrystalline polymers: 2” *Polymer*, vol. 28, pp. 1534-1542, 1987.

[85] L. C. E. Struik, “The mechanical and physical ageing of semicrystalline polymers: 3. Prediction of Long Term Creep from Short Time Tests” *Polymer,* vol. 30, pp. 799-814. 1989

[86] L. C. E. Struik, “The mechanical and physical ageing of semicrystalline polymers: 4” *Polymer*, vol. 30, pp. 815-830. 1989.

[87] J. A. White, *et al.*, "Ergogenic demands of a 24 hour cycling event," *British Journal of Sports Medicine,* vol. 18, pp. 165-171, September 1, 1984.

[88] J. White, “Silver recovery--departmental management approach”, *Radiography,* vol. 46, pp. 35-41, 1980.

[89] J. White, “The site model theory and the standard linear solid”, *Rheologica Acta,* vol. 20, pp. 23-28, 1981.

[90] J. R. White, “Site-Model Theory of Nonlinear Viscoelasticity”, *Journal of Polymer Science,* vol. 19, pp. 1371-1376, 1981.

[91] J. R. White, “On Internal Stress and activation volume in polymers”, *Journal of Material Science,* vol. 16, pp. 3249-3262, 1981.

[92] B. Haworth and J. R. White, “Some Measurements of Internal Stress and Activation Volume in Acrylic Polymers”, *Journal of Material Science,* vol. 16, pp. 3263-3274, 1981.

[93] M. Thormpson, J. R. White, “Effect of a Temperature Gradient on Residual Stresses and Distortion in Injection Moldings”, *Polymer Engineering and Science,* vol. 24, pp. 227-241, 1984.

---

[94] G. J. Sandilands and J. R. White, “Effect of Aging on Internal Stress and Fatigue Fracture of Poly(4-Methyl Pentene-1)”, *Journal of Applied Polymer Science,* vol. 30, pp. 4771-4792, 1985.

[95] D. Ryan, (2008, August 17), “Annealing of Polyethylene Pipe”, *Akatherm,* [Online]. Available: http://www.akatherm.com/files/Annealing%20polyethylene%20pipe.pdf

[96] C. Vasile and M. Pascu, “Properties”, *Practical Guide to Polyethylene,* Shrewsbury, UK: Rapra Technology Ltd. , 2005, pp 38

[97] A. L. Kovarski, “Effect of Polymer Structure and Physical State”, *Molecular dynamics of additives in polymers,* Zeist, The Netherlands: VSP BV, 1997, pp. 212.

[98] S. Tiemprateeb, *et al.*, "A comparison of degree of properties enhancement produced by thermal annealing between polyethylene and calcium carbonate-polyethylene composites," *Polymer Testing,* vol. 19, pp. 329-339, 2000.

[99] J. Suwanprateeb, K.E. Tanner, S. Turner and W. Bonfield, “Influence of Sterilization by Gamma Irradiation and of Thermal Annealing on Creep of Hydroxyapatite-Reinforced Polyethylene Composites”. *J Biomed Mater Res* , vol. 39, pp. 16–22. 1998.

[100] J. Foreman, “Dynamic mechanical analysis of polymers”, in *TA 236,* Amerian Laboratory,1997.

[101] “ASTM D4065-06 Standard Practice for Plastics: Dynamic Mechanical Properties: Determination and Report of Procedure,” ASTM International, West Conshohocken, PA, 2010, DOI: 10.1520/D4065-06, www.astm.org.

[102] G. W. Kamykowski, “Rheology Fundamentals and Testing on a Q800 DMA”, TA Instruments, March 16, 2010

[103] “.DMA Q800”, TA Instruments, [Online], Available: http://www.tainstruments.com/product.aspx?siteid=11&id=25&n=1

[104] “TA Instruments Dynamic Mechanical Analyzer DMA Q800 Getting Started Guide”, TA Instruments, www.tainstruments.com

[105] “Material Safety Data Sheet: Treated-FL” *Omya*, [online]: Available: http://www.omya-na.com/C12574E100398A1C/vwLookupImagesforLoad/USFL_M04_Treated_ftfl.pdf/$File/USFL_M04_Treated_ftfl.pdf.

[106] “Introduction to Dynamic Mechanical Analysis (DMA): A Beginner’s Guide”, *Perkin Elmer*, [Online], Available: http://las.perkinelmer.com/Content/manuals/gde_introductiontodma.pdf

APPPENDICES

VITA

Reaj Uddin Ahmed

Candidate for the Degree of

Master of Science

Thesis: ANALYZING AND IMPROVING VISCOELASTIC PROPERTIES OF HIGH DENSITY POLYETHYLENE

Major Field: Mechanical and Aerospace Engineering

Biographical: Born in Dhaka, Bangladesh on September 22, 1986.

Education: Received B. S. degree in Mechanical Engineering from Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh on March 2009.

Completed the requirements for the Master of Science in Mechanical and Aerospace Engineering at Oklahoma State University, Stillwater, Oklahoma in July, 2011.

Experience: Graduate Research Assistant in Mechanical and Aerospace Engineering Department, Oklahoma State University, Stillwater, Oklahoma
August, 2009-May,2011.

Graduate Teacher's Assistant in Mechanical and Aerospace Engineering Department, Oklahoma State University, Stillwater, Oklahoma
August, 2009-December,2010

Name: Reaj Uddin Ahmed Date of Degree: July, 2011

Institution: Oklahoma State University Location: Stillwater, Oklahoma

Title of Study: ANALYZING AND IMPROVING VISCOELASTIC PROPERTIES OF HIGH DENSITY POLYETHYLENE

Pages in Study: 100 Candidate for the Degree of Master of Science
Major Field: Mechanical and Aerospace Engineering

High Density Polyethylene (HDPE) is closely packed, less branched polyethylene having higher mechanical properties, chemical resistance, and heat resistance than Low Density Polyentylene (LDPE). Better properties and cost effectiveness make it an important raw material over LDPE in packaging industries. Stacked containers made of HDPE experience static loading and deformation strain during their storage period in a warehouse. As HDPE is a viscoelastic material, dimensional stability of stacked HDPE containers depends on time dependent properties such as creep and stress relaxation. Now, light weighting is a driving force in packaging industries, which results in lower production costs but performance of the product becomes a challenge. Proper understanding of the viscoelastic properties of HDPE, with relevant FE simulation can facilitate improved designs.

This research involves understanding and improving viscoelastic properties, creep behavior, and stress relaxation of HDPE. Different approaches were carried out to meet the objectives. Organic filler $CaCO_3$ was added to HDPE at increasing weight fractions and corresponding property changes were investigated. Annealing heat treatments were also carried out for potential property improvements. The effect of ageing was also investigated on both annealed and non annealed HDPE. The related performance of different water bottles against squeeze pressure was also characterized.

Both approaches, incorporation of $CaCO_3$ and annealing, showed improvements in the properties of HDPE over neat HDPE. This research aids finding the optimum solution for improving viscoelastic properties, stress relaxation, and creep behavior of HDPE in manufacturing.

ADVISER’S APPROVAL: Dr. Jay C. Hanan