Rheology of ‘Green’ Plasticizers: Application of Time-Temperature Superposition

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Abstract

Plasticizers are small organic molecules that are blended with plastics in order to increase their workability and flexibility, thereby making the plastics more processable. Around 90% of all plasticizers are used to plasticize poly(vinyl) chloride (PVC), with di(2-ethylhexyl phthalate) (DEHP) being the most common PVC plasticizer. Plasticizers are not chemically bound to the polymer and therefore tend to leach into the environment and are of increasing concern to human health. DEHP belongs to a class of compounds known as phthalates, which have been found to induce a wide range of developmental and reproductive toxicities in mammals and are suspected endocrine disruptor in humans. As such, there has been an effort to synthesize new ‘green’ plasticizers, with more favorable biodegradation behaviour.

It is important to ensure that these ‘green’ plasticizers have comparable mechanical properties to their commercial counterparts. My thesis research aimed to document the rheological behaviour of PVC plasticized with our ‘green’ plasticizers and compare the results to the rheological behaviour of PVC plasticized with commercially available plasticizers including DEHP. The rheological behaviour was characterized using dynamic mechanical analysis and discrete relaxation time spectra. The technique of time-temperature superposition was used to extend the measurement range of the experiments and to produce master curves for each plasticizer. The effect of changing the molecular structure of the plasticizer molecules was studied and it was found that increasing the alkyl chain length in the central dibenzoate structure of benzoate-based plasticizers and in the side chains of the succinate structure in succinic acid derived plasticizers had no effect on the rheological responses of the materials under our test conditions. The viscoelastic master curves of the elastic and viscous moduli, G' and G", respectively, for the ‘green’ plasticizers compared favourably to those of the commercial plasticizers, and therefore it was concluded that the ‘green’ plasticizers exhibited similar rheological behaviour to the commercial plasticizers, as seen by the comparable shape of their master curves. PVC plasticized with 1,4 butanediol dibenzoate (1,4 BDDB) exhibited lower storage modulus values than its commercial counterparts and therefore, 1,4 BDDB was chosen as the best performing ‘green’ plasticizer under our test conditions.

Résumé

Les plastifiants sont des molécules organiques qui sont ajoutées aux matières plastiques afin d’augmenter leur souplesse et flexibilité (élasticité) et afin d'améliorer leurs capacités de traitement. Environ 90% des plastifiants sont utilisés comme plastifiants de poly(chlorure de vinyle) (PVC), avec phthalate de (di-2-éthylhexyle) (DEHP) étant le plus commun. Les plastifiants ne sont pas liés chimiquement au polymère et conséquemment se libèrent dans l’environnement, présentant plusieurs dangers pour la santé humaine. En effet, DEHP appartient à une classe de composés connus comme les phthalates, dont leur toxicité est assez bien documentée. Les phthalates peuvent causer un large éventail de problèmes développementaux et reproductifs chez les mammifères, et sont soupçonnés d’être perturbateurs endocriniens chez les humains. Par conséquent, la synthèse de nouveaux plastifiants « verts », avec une biodégradation plus favorable, se trouve de plus en plus nécessaire.

Cependant, avant de pouvoir remplacer les plastifiants nocifs couramment utilisées, il est important d’assurer que les plastifiants «verts» ont des propriétés mécaniques comparables à leurs homologues commerciaux. Ma thèse de recherche vise à documenter le comportement rhéologique du PVC plastifié avec nos plastifiants «verts» et de comparer les résultats au comportement rhéologique du PVC plastifié avec des plastifiants disponibles dans le commerce incluant le DEHP. Le comportement rhéologique a été caractérisé en utilisant la méthode d’analyse mécanique dynamique et des spectres discrets de temps de relaxation. Le principe d’équivalence temps-température a été utilisé pour étendre la plage de mesure des expériences et pour produire des courbes maîtresses pour chaque plastifiant. L'effet de modifier la structure moléculaire des plastifiants a été étudié. Il a été constaté que l'augmentation de la longueur du groupe alkyle dans la partie centrale de la structure du dibenzoate et dans les chaînes latérales de la structure du succinate n’avait aucun effet sur la réponse rhéologique des matériaux. Les courbes maîtresses viscoélastiques G' et G" pour les plastifiants «verts» se comparent favorablement à ceux des plastifiants commerciaux. Il a donc été conclu que les plastifiants «verts» ont un comportement rhéologique similaire aux plastifiants commerciaux, et peuvent être considérés comme remplacements prometteurs. PVC plastifié avec 1,4 butanediol dibenzoate (1,4 BDDB) a produit des valeurs de module de conservation inférieures à ses homologues commerciaux, et donc 1,4 BDDB a été choisi comme le meilleur plastifiant «vert».

Acknowledgements

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I would also like to thank the members of both of my lab groups for their frequent help and support throughout my work. In particular, I would like to thank Hanno Erythropel for training me in many of the experimental techniques that I used throughout my work, and for providing me with the 'green' plasticizers that he synthesized. I would also like to thank Daniel Burkat for designing a MATLAB code to perform time-temperature superposition. A big thank you as well to Melissa Dick and Thomas Vlasic who read my manuscript numerous times and provided me with invaluable feedback.

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Contribution of Authors

The following manuscript was primarily the work of this author with contributions by Daniel Burkat, Hanno Erythropel, Dr. Milan Maric, and Dr. Richard Leask.

Daniel Burkat developed the MATLAB program used to apply time-temperature superposition to the raw data to produce viscoelastic master curves. Hanno Erythropel synthesized all of the ‘green’ plasticizers used in this work and aided in the extrusion of plasticized PVC samples.

Dr. Milan Maric and Dr. Richard Leask helped develop the experimental setup and edited the manuscript.

Introduction

Introduction to Plasticizers

Plasticizers are small organic molecules that are blended with plastics in order to increase their workability and flexibility, as well as improve their processing capabilities. They work by decreasing the glass transition temperature (T_g) of the plastic materials to which they are added[1].

Around 90% of plasticizers are used to plasticize poly(vinyl) chloride (PVC), with di(2-ethylhexyl phthalate) (DEHP) being the most common PVC plasticizer[2]. DEHP is found in many products ranging from building materials, cosmetics, imitation leather, and food packaging to medical tubing and bags[3]. DEHP belongs to a class of compounds known as phthalates, which have been the subject of increased study in recent years due to their suspected adverse health effects. The primary metabolite of DEHP, mono(ethylhexyl phthalate) (MEHP), has been found to induce a wide range of developmental and reproductive toxicities in mammals and is a suspected endocrine disruptor in humans[4]. Between 2004 and 2008 the European Parliament, U.S. Congress, and Health Canada issued regulations aimed to limit phthalate exposure in the general population, and particularly in vulnerable groups such as infants, whose growth and development can be significantly impacted by endocrine disrupting compounds[5-7].

DEHP is blended with PVC in concentrations of up to 60 wt% and is not chemically bound to the polymer[8]. The alarming abundance of DEHP in the environment is reflected in its detection in soil, air, and water, as well as human urine[9, 10]. Studies have shown that medical procedures such as blood transfusions and hemodialysis comprise the largest source of exposure to DEHP, producing intravenous exposure levels significantly higher than those found in the general population[11]. Following medical exposure, food products are the greatest source of

DEHP exposure[12]. Due to the widespread use of the plasticizer and its tendency to leach into the environment, there has been increasing concern about the threat posed by DEHP exposure to human health. As such, there has been an effort at McGill University to synthesize new ‘green’ plasticizers, with more favorable biodegradation behaviour, that do not pose a significant risk to human health. Several compounds, with structural similarities to DEHP have been proposed by our group[13-15], and can be seen in Figure 1, along with DEHP.

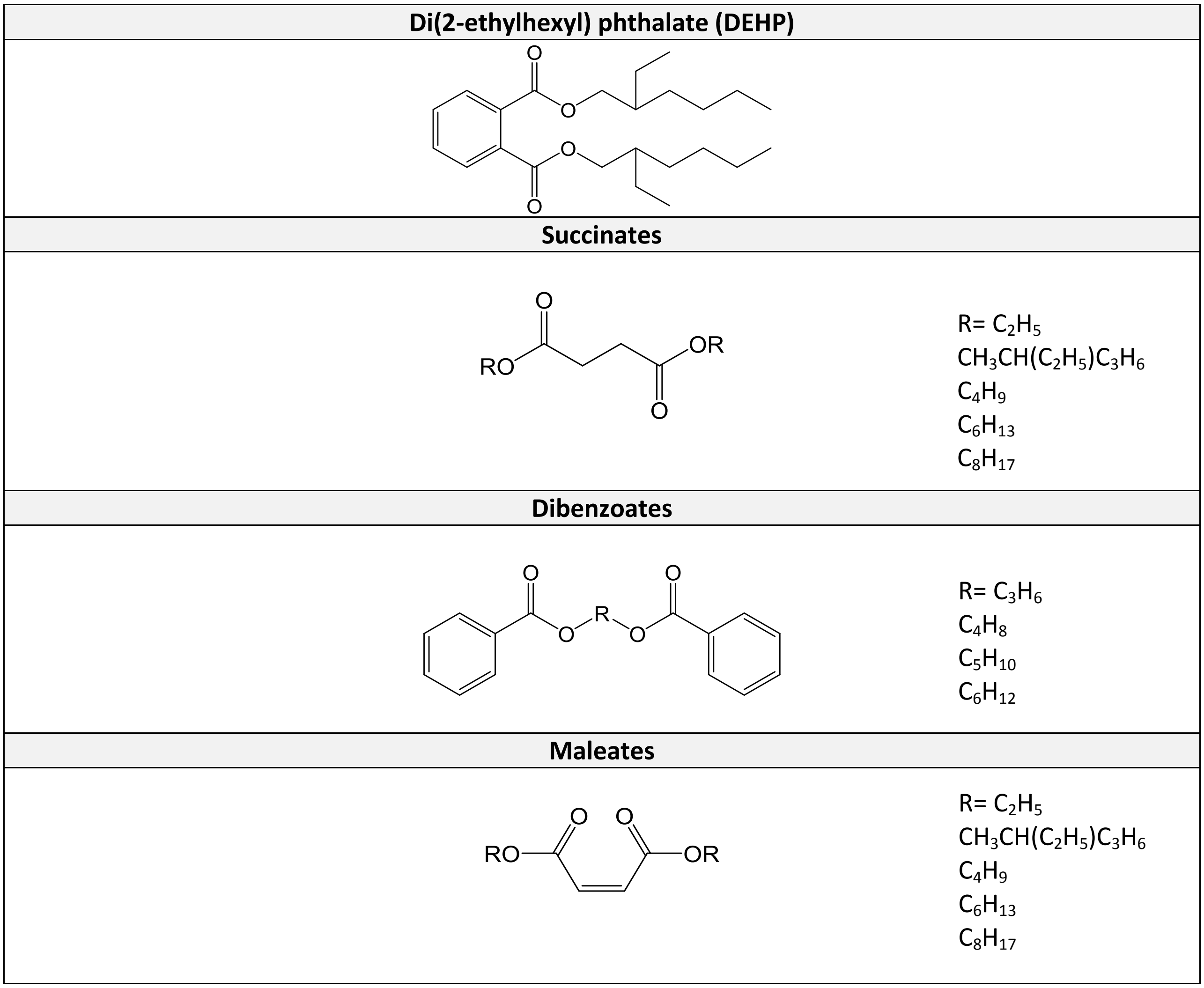

Figure 1: Molecular structures of the commercially available plasticizer, DEHP, as well as 14 new ‘green’ plasticizers synthesized at McGill University

It is important to ensure that these ‘green’ plasticizers have comparable mechanical properties to their commercial counterparts so that they can effectively and easily replace DEHP both during processing, and for end-use applications.

Rheology and Time-Temperature Superposition

Rheology

Rheology is the study of the flow and deformation of matter[16]. Two of the simplest linear relations between force and deformation in solids and liquids are Hooke’s law and Newton’s law of viscosity, respectively. Hooke’s law states that force is proportional to deformation in an elastic solid while Newton’s law states that stress is proportional to the rate of strain applied to a viscous fluid. In practice, the study of rheology is restricted to the study of materials with non-linear dependencies between force and rate of deformation, in other words, materials that exhibit behaviour that lies somewhere between that of a perfectly elastic solid and a Newtonian fluid[17]. Many scientifically relevant materials, including polymers such as PVC, behave in this manner and are described as being viscoelastic. As such, rheology can be used to study the relationships between force and deformation in these materials.

One of the goals of rheological study is to establish relationships between applied forces and the effects induced by these forces, known as constitutive relationships. Another goal is to establish relationships between the observed rheological properties of a material and its composition or molecular structure. The latter is of importance in chemical process control and quality control[16].

This research primarily involves the use of rheometry to relate the rheological properties of PVC to its composition. The rheological properties of PVC plasticized with various ‘green’ plasticizers were compared to DEHP in order to compare plasticizer performance.

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) is an experimental technique that can be used to obtain important information about viscoelastic material properties such as stiffness and viscous damping. DMA involves the application of a small periodic deformation to a sample, at varying angular frequencies and constant amplitude. Specifically, a sinusoidal time-varying strain (or stress) is applied, and the resultant stress (or strain) is measured[18]. The strain input can be represented by Equation 1.

$$\gamma = \gamma_o \sin \omega t \qquad \text{[Equation 1]}$$

γ [dimensionless,%] represents the strain function, γ_o [dimensionless,%] represents the strain amplitude, ω [rad/s] represents the angular frequency, and t [s] represents time.

Due to the time-dependent relaxation exhibited by viscoelastic materials, the response will oscillate at the same frequency as the input, but will be out-of-phase with the applied stimulus. The stress response can be represented by Equation 2.

$$\tau = \tau_o \sin (\omega t + \delta) \qquad \text{[Equation 2]}$$

τ [Pa] represents the stress function, τ_o [Pa] represents the stress amplitude, ω [rad/s] represents the angular frequency, t [s] represents time, and the phase angle δ [rad] represents the shift in the stress response compared to the strain input.

In *purely elastic* materials, it is expected that the material response will be in phase with the stimulus, resulting in $\delta = 0°$. In a *purely viscous* material, the response is expected to be out of phase with the stimulus, with $\delta = 90°$. A viscoelastic material exhibits a phase angle of between 0° and 90°[19].

The results of a dynamic experiment can be expressed in terms of the complex modulus of the material, which can be resolved into a storage modulus (G') and loss modulus (G"). By decomposing the stress wave into two components, one for the in-phase response, G', and one for the out-of-phase response, G", the storage and loss moduli of the material, representing the elastic and viscous responses, respectively, can be computed, as seen in Equation 3. The loss modulus can be thought of as a measure of the material damping or energy loss (as heat, for example), while the storage modulus can be thought of as the energy stored in the material or the stiffness of the material[17].

$$\tau \;=\; G' \gamma_o \, sin \, \omega t \;+\; G'' \gamma_o \, cos \, \omega t \qquad \text{[Equation 3]}$$

G' [Pa], the in-phase response, represents the storage modulus, and G" [Pa] the out-of-phase response, represents the viscous (or loss) modulus.

These dynamic moduli have been found to change with temperature, and performing DMA over a range of temperatures can be used to study important molecular transitions within a material. Furthermore, when experiments are run with small amplitude deformations, it can be assumed that the material is in the linear elastic region, where stress is proportional to strain and material response is independent of the applied amplitude[18]. The application of small amplitudes also reduces inertial effects. Additionally, using small amplitudes allows for the application of time-temperature superposition to extend the data range[20].

Time-Temperature Superposition

One of the important phenomena observed in viscoelastic materials is the time-dependence of the material response. For polymers, the elastic modulus of the material decreases with increasing time under an applied load[17]. The concept of ‘corresponding states’ proposes that if the relaxation times in a given material response process have the same temperature dependence, the melt flow properties at a certain time and temperature are equivalent to flow properties at a longer time and lower temperature. Thus, time and temperature have equivalent effects on molecular motion and on the viscoelastic properties of a material. This equivalency forms the basis of time-temperature superposition[18].

In engineering practice, materials are often designed for use over long periods of time (for example, several decades) based on data obtained from experiments performed over much shorter time scales. While it is necessary to obtain data regarding common design parameters, such as the elastic modulus, over the proposed lifetime of the material, obtaining data over such long time scales can be expensive and experimentally impractical. Similarly, for certain materials it is desirable to obtain viscoelastic data for very small time scales, which can be equally difficult to measure due to inertia and other mechanical limitations of laboratory equipment[21]. Time-temperature superposition is an empirical method that can be used for amorphous polymers to estimate short-term and long-term behaviour of the material that cannot be easily measured, by relating the material flow properties at different temperatures to different times at a single reference temperature. Therefore, by performing experiments at different temperatures, it is possible to use the concept of time-temperature equivalency to shift material properties along the time (or frequency) axis, around a reference temperature, effectively extending the time scale over which values are obtained[17]. An example of curve shifting to produce a master curve is shown in Figure 2.

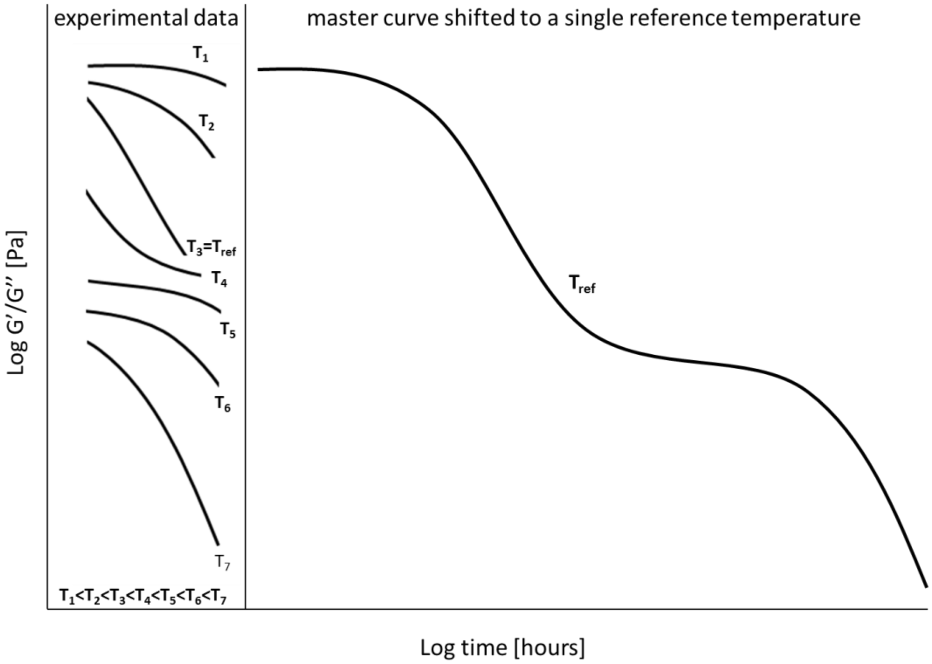

Figure 2: An example of the use of time-temperature superposition to produce a single master curve of modulus versus time at a reference temperature (adapted from Tobolsky et. al.[22])

There are two approaches to shifting experimental curves in order to create a single master curve. The first approach is known as 'free shifting', where shift factors are determined by manually shifting data until they appear to superimpose. In this approach, multiple shift factors are derived independently for every master curve. This method is preferred for materials with unknown or poorly characterized temperature and frequency responses, since the underlying shape of the data guides the overall shape of the master curve. The second approach is known as 'constrained shifting', where an underlying model is assumed and is used to compute shift factors that fit a predicted functional form[20]. Two common relationships used to describe the effect of temperature on the horizontal shift factor are the Arrhenius and Williams-Landel-Ferry (WLF) equations[18].

The Arrhenius model is used to correlate the time and temperature behvaiour of amorphous polymers outside of the glass transition region. Shift factors can be computed using Equation 4[18]:

$$a_T(T) = exp\left[\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \qquad \text{[Equation 4]}$$

The shift factor, a_T, represents the constant quantity by which the viscoelastic properties at each temperature are divided in order to shift the curves along the time axis until consecutive curves overlap. E_a is the activation energy for flow, R is the gas constant, T is the experimental temperature, and T_{ref} is the reference temperature at which the master curve is produced.

The WLF equation has been proven to be successful in the glass transition region, from T_g until approximately T_g +100°C, as shown in Equation 5[16].

$$\log(a_T) = \frac{-C_1(T-T_{ref})}{C_2+(T-T_{ref})} \qquad \text{[Equation 5]}$$

Here, a_T is the horizontal shift factor, T_{ref} is the reference temperature at which the master curve is produced and C_1 and C_2 are empirical constants.

In most instances encountered in literature where time-temperature superposition is performed, the material behaviour can be reduced to the WLF equation. In this research, time-temperature superposition is used to extend the time-scale of elastic modulus measurements, producing a master curve for each plasticizer. Since experimental temperatures are more than 100°C above T_g, the shift factors will be fit to an Arrhenius model.

Discrete Relaxation Spectra

In theory, the relaxation spectrum calculated from a material's rheological properties is thought to reflect the molecular dynamics and molecular structure of the material. In practice, relaxation spectra are often used to calculate numerous material functions that can be used for engineering calculations (eg. long-time failure analysis) and in modelling polymer processing applications[16].

Based on a multi-mode Maxwell model, discrete representations of the storage and loss moduli can be derived, as seen in Equations 6 and 7[23].

$$G'(\omega) = \sum_{i=1}^{N} g_i \frac{\omega^2 {\lambda_i}^2}{1+\omega^2 {\lambda_i}^2} \qquad \text{[Equation 6]}$$

$$G''(\omega) = \sum_{i=1}^{N} g_i \frac{\omega \lambda_i}{1+\omega^2 {\lambda_i}^2} \qquad \text{[Equation 7]}$$

G' [Pa] and G" [Pa] are the frequency-dependent storage and loss moduli, respectively. g_i [Pa] is the corresponding elastic modulus of the relaxation time λ_i [s], and ω [rad/s] is angular frequency.

These equations can be fit to experimental G' and G" data, obtained through linear viscoelastic tests at discrete frequencies. An objective function can then be formulated, containing the experimental G' and G" values, as well as those determined by fitting to the model. The discrete relaxation times are calculated by minimizing this objective function. Calculation of the relaxation spectrum is known as an ‘ill-posed problem’, meaning that it does not have a unique, well-defined solution for all data. Therefore, obtaining a numerical solution is difficult since small changes in data can lead to large changes in the solution. The problem can be reformulated, using a technique known as ‘regularization’, allowing for the discrete spectrum to be solved[23].

Known Plasticized PVC Properties

The rheological behaviour of PVC melts plasticized with DEHP, and specifically, the effect of DEHP concentration, has previously been investigated by Zou et. al.[24]. They found that with increasing DEHP concentration, G' and G" decreased. They also found that at lower plasticizer concentrations, G' was greater than G", indicating a solid-like material response while at higher plasticizer concentrations, G" was greater than G', indicating a liquid-like response. As plasticizer concentration was increased, the rheological behaviour of the material suggested a solid-liquid transition.

Firlotte et. al. previously characterized the T_g and tensile strength of PVC blended with the ‘green’ dibenzoate plasticizer, 1,5 pentanediol dibenzoate (1,5 PDDB), and compared it to commercial plasticizers, including DEHP[25]. They found that the T_g of PVC blended with 1,5 PDDB was the same as for the commercial plasticizer di(ethylene glycol) dibenzoate (DEGDB) at all plasticizer concentrations, while it was higher than that of DEHP at concentrations greater than 16.6 wt%. The tesile strength of 1,5 PDDB was found to be similar to DEHP. The effect of plasticizer concentration on tensile properties was also investigated and it was found that as DEHP concentration was increased, the tensile strength of the material decreased. It was also found that T_g decreased with increased plasticizer concentration.

Erythropel et. al. investigated the T_g and tensile properties of PVC blended with di(2-ehtylhexyl)-terminated ‘green’ plasticizers, compared with DEHP[13]. Four families of ‘green’ plasticizers, fumarates, maleates, succinates and adipates, were studied. The PVC blends produced with the succinate and maleate plasticizers were found to have lower T_g values than DEHP. The succinate plasticizers were also found to demonstrate comparable elongation at break to DEHP and have a lower Young's modulus than DEHP, at plasticizer concentrations above 30 wt%.

Erythropel et. al. further investigated the effect of alkyl chain length and central structure on the T_g of succinate-based plasticizers[14]. They found that increasing chain length resulted in a decrease in T_g, while branching had no effect on T_g. PVC blended with dihexyl 4-methyl cyclohexane-1,2-dicarboxylate (DHMCH) and dihexyl cyclohexylsuccinate (DHCHS), which have bulky central groups, were found to have significantly lower T_g values than dihexyl succinate (DHS) and dihexyl methylsuccinate (DHMS), which do not contain aromatic rings in their central structure.

Objectives and Hypotheses

This thesis research aims to characterize and compare the rheological behaviour of PVC plasticized with 'green' plasticizers versus PVC plasticized with commercially available plasticizers such as DEHP, through dynamic mechanical analysis. Using time-temperature superposition, rheological master curves will be produced for each PVC-plasticizer blend using data collected over a range of temperatures and frequencies. Characterizing the viscoelastic response of the material at elevated temperatures and over a wide range of frequencies is important for polymer processing applications (e.g. for the determination of optimum processing conditions).

This study also aims to investigate the effect of plasticizer molecular structure on the rheological properties of plasticized PVC blends. Specifically, the effect of alkyl chain length in the central structure and side chains of various plasticizers is investigated. It is hypothesized that increasing alkyl chain length in the plasticizer molecules will improve their plasticizing ability by increasing the separation between PVC chains, leading to greater chain mobility, and consequently a more flexible material.

Materials and Methods

Test discs containing 40 parts per hundred rubber (PHR) plasticizer were produced through extrusion and heat pressing at high temperatures. Oscillatory shear data was then obtained for each plasticized disc through rheometry.

PHR is a common way to express additive concentration in the rubbers industry. The concentration of the additives is expressed as a mass fraction of the rubber material[26].

Extrusion of PVC-Plasticizer Blends

All PVC-plasticizer blends were prepared to a final concentration of 40 PHR (28.6 wt%) plasticizer using a twin-screw extruder (Haake Minilab, Thermo Electron Corporation). Unplasticized PVC (Solovay Benvic, France) was also combined with epoxidized soy bean oil (Chemtura Corporation), a thermal stabilizer that prevents PVC degradation during processing, and stearic acid (Fisher Scientific), a lubricant that ensures smooth and continuous flow through the extruder.

The extruder was operated between 120°C and 130°C (depending on plasticizer concentration in the blend), with a batch size of 3 g, and a screw rotation speed of 15 min^{-1}. A 20 PHR (16.7wt%) plasticizer blend was first extruded at 130°C and then combined with additional plasticizer at 120°C to achieve a concentration of 40 PHR. The 20 PHR blend was prepared with 4 PHR epoxidized soy bean oil and 5 PHR stearic acid. The extrusion was performed in two steps to ensure that the maximum liquid plasticizer load in the extruder allowed for effective mixing with the dry feed ingredients.

After the desired number of batches was extruded, the extrudate was cut into small pellets and recycled through the extruder, to produce a homogeneous blend.

Preparation of Test Discs by Heat Pressing

The plasticized PVC was pressed into circular discs of 1 mm thickness using a heat press (Carver Manual Hydraulic Press with Watlow Temperature Controllers, Carver). The extrudate was cut into small pellets and used to fill a stainless steel mould with circular cutouts. The press was heated to a temperature of 140°C and the mould, placed between two stainless steel plates, was inserted into the press. A pressure of 1 MPa was applied for 10 min, after which the mould was degassed three times, and then a pressure of 2 MPa was applied for 10 min, followed by a pressure of 3 MPa for 15 min. The plates were then cooled, using the cooling water system, and the cooled discs were removed from the mould. The discs were placed in a desiccator (Drierite, Fisher Scientific, Montréal, QC) for a minimum of 48 hours, or until needed for testing.

Rheology

Oscillatory shear tests were performed using a strain-controlled rheometer (Anton Paar MCR 302) with parallel plate geometry (25 mm plate diameter) and a CTD 450 convection oven attachment, under a nitrogen environment. A strain amplitude within the linear viscoelastic range (5%) was applied over a frequency range of 0.3-300 rad/s. A temperature sweep was performed between 110°C and 200°C, with measurements taken every 10°C. The storage modulus (G') and loss modulus (G") were automatically reported by the Anton Paar Rheoplus software. The data obtained from the tests was used to produce rheological master curves using time-temperature superposition.

Time-Temperature Superposition

A time-temperature superposition algorithm was used to produce rheological master curves and extend the frequency range of the measurements[27]. The G' and G" isotherms were shifted horizontally along the x-axis, with respect to a reference temperature (T_o=140°C), with each shift factor being independently calculated to ensure the best overlap with adjacent isotherms. The best overlap between curves was determined by a method of least squares. The viscoelastic properties of the material are measured at a temperature (T) and angular frequency (ω). The measured angular frequency is multiplied by a shift factor (a_T), in order to determine the material properties at the desired reference temperature (T_o). The shifted curves can be expressed by Equation 8.

$$G'(T, \omega a_T) = G'(T_o, \omega) \qquad \text{[Equation 8]}$$

G' represents the storage modulus (however this relationship holds for number of other polymer melt flow properties as well), T represents the temperature at which a measurement was taken, ω represents the angular frequency at which a measurement was taken, T_o represents the reference temperature to which all curves are shifted, and a_T represents the temperature-dependent horizontal shift factor.

Discrete Relaxation Spectra

In order to compute the discrete relaxation spectra from the experimental G' and G", a computer program developed by Takeh et. al. was used[28]. The program applied a nonlinear Tikhonov regularization and used the Levenberg-Marquardt method to solve the mathematically ‘ill-posed’ problem and obtain the relaxation spectrum[29].

Statistics

Statistical analysis was performed using GraphPad Prism software. An unpaired 1-tailed t-test was used at a 95% confidence interval. The t-test was performed at three frequencies that were chosen from the low, medium, and high range of the master curve.

Results

Dynamic Mechanical Analysis

Frequency Dependence of G' and G'' (PVC-DEHP)

An example of DMA results obtained through frequency and temperature sweeps for a PVC-DEHP blend is shown in Figure 3. The data is presented as the log of the modulus versus the log of the oscillation frequency. Runs at different temperatures (110°C-200°C) are plotted on the same graph. It can be seen that with increasing temperature, the storage and loss moduli of the material decrease. Conversely, the storage and loss moduli increase with increasing frequency. The same trend was seen for all of the plasticizers studied.

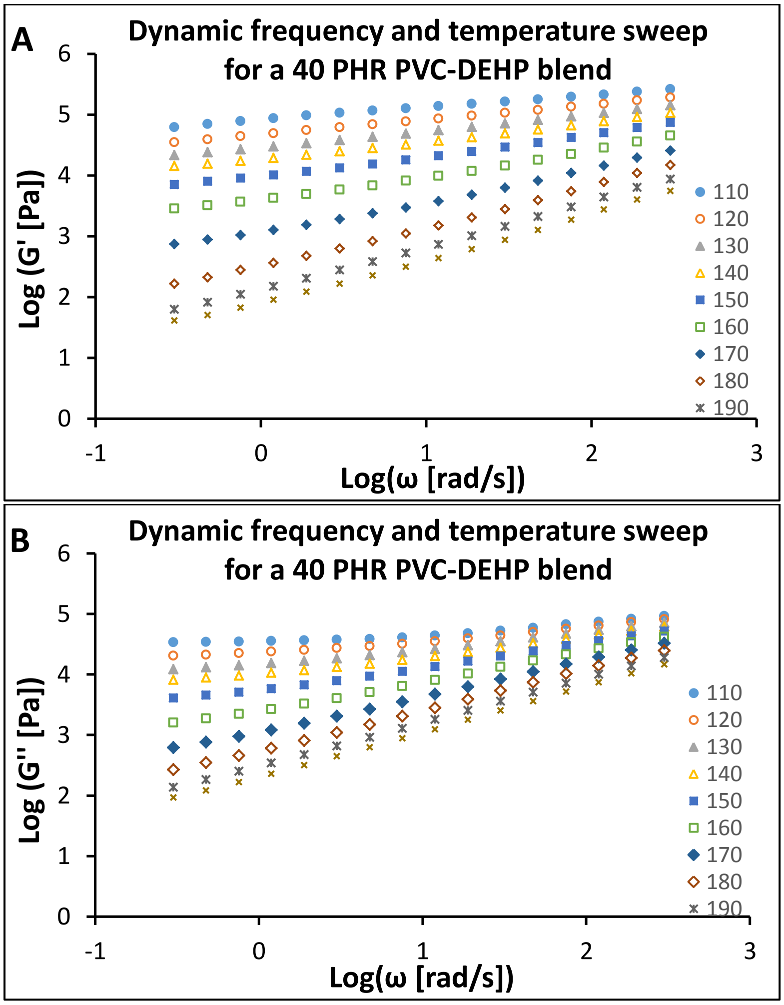

Figure 3: Dynamic frequency sweep for a sample of 40 PHR PVC-DEHP, from T=110°C to 200°C. (A) Storage modulus, G' (B) Loss modulus, G''

Time-Temperature Superposition

Dynamic viscoelastic master curves were produced by horizontally shifting G' and G" along the frequency axis. In Figure 4, the storage modulus, G', was plotted against the shifted frequency for a PVC-DEHP system. Visually, it can be seen that the shifted isotherms generally overlap well, producing a continuous curve, demonstrating a successful superposition. The weakest overlap is observed at the low frequency range of the data at high temperatures. The temperature dependence of the horizontal shift factor is shown in Figure 5, and can be seen to fit well to an Arrhenius model. Similar trends in isotherm overlap were observed for all of the plasticizers.

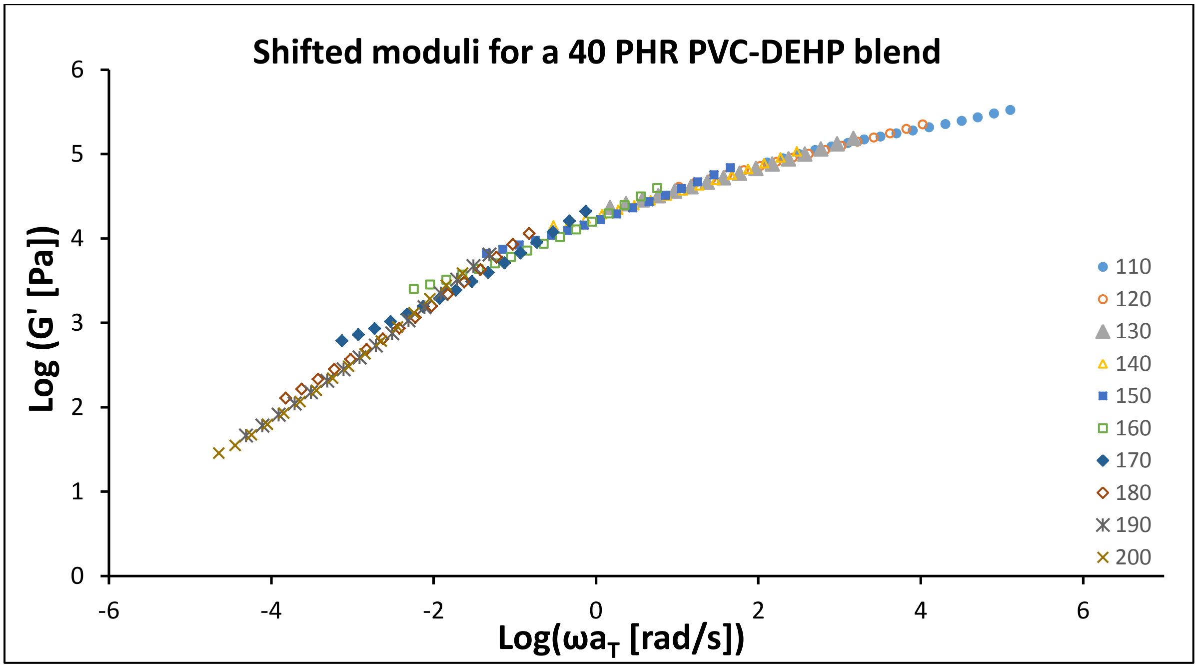

Figure 4: Dynamic viscoelastic master curve, prepared through time-temperature superposition, for a 40 PHR PVC-DEHP blend at T_{ref}= 140 °C

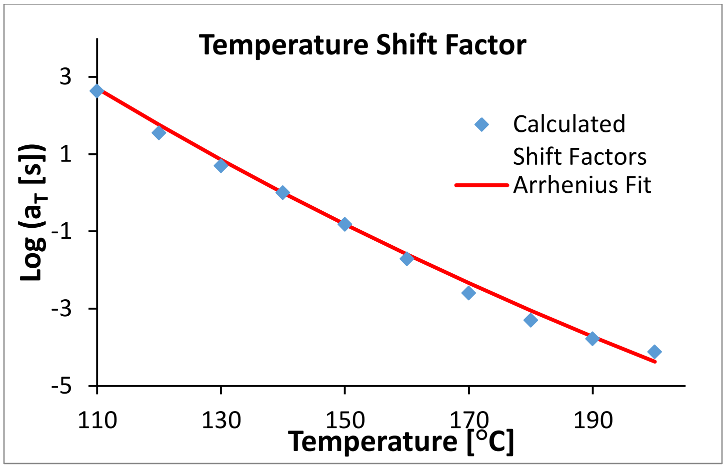

Figure 5: Temperature dependence of horizontal shift factors determined through time-temperature superposition, compared with Arrhenius fit for a 40 PHR PVC-DEHP blend. a_T is the shift factor given in Equation 4

Dynamic Viscoelastic Master Curves of G' and G''

In Figures 6-9, the viscoelastic master curves of G' and G" are shown for the green plasticizers, dioctyl succinate (DOS) and 1,4 butanediol dibenzoate (1,4 BDDB), as well as for the commercial plasticizers, DEHP and DINCH. Each curve is the average of three runs done from three different batches (except 1,4 BDDB which has an n=2). DOS and 1,4 BDDB were selected among the 14 ‘green’ plasticizers based on preliminary results from a collaborative study as part of a CIHR Team Grant[13]. They were found to be the two most promising ‘green’ plasticizers in terms of their toxicity in mammalian cells. All four PVC-plasticizer blends exhibit an increase in modulus with increasing frequency. It can also be seen that in all four cases, G" increases more steeply than G' at low frequencies, and then exhibits a slight decrease in slope, so that the two curves never cross (i.e. G" is never higher than G'). A visual comparison of the G' curves and G" curves shows a similar shape for all four plasticizer blends.

Figure 6 shows very good batch-to-batch reproducibility for PVC-DEHP, evidenced by the small standard deviation seen in the error bars. It can also be seen that over the entire frequency range of the master curve, G' is higher than G" with the two curves approaching each other at higher frequencies.

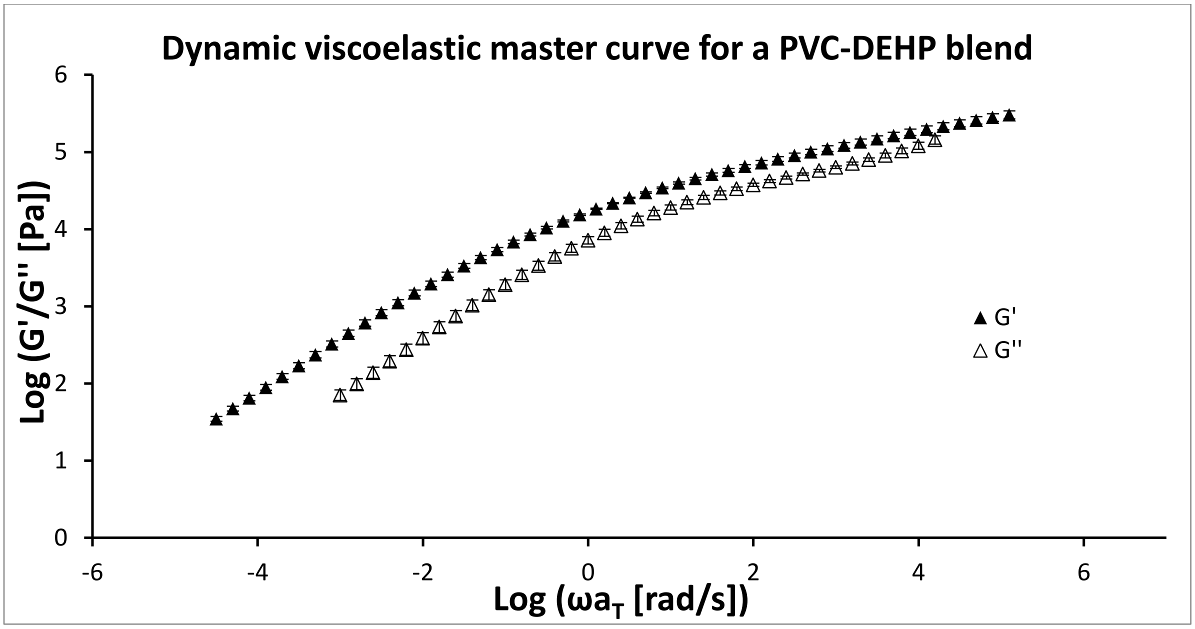

Figure 6: Dynamic viscoelastic master curves (G', G''), prepared through time-temperature superposition, for a 40 PHR PVC-DEHP blend at T_{ref}= 140 °C. Error bars represent standard deviation, n=3

Figures 7 and 8 show slightly greater batch-to-batch variability for PVC-DINCH and PVC-DOS compared with PVC-DEHP. It can also be seen that for both plasticizer blends, G" reaches G', but never crosses it.

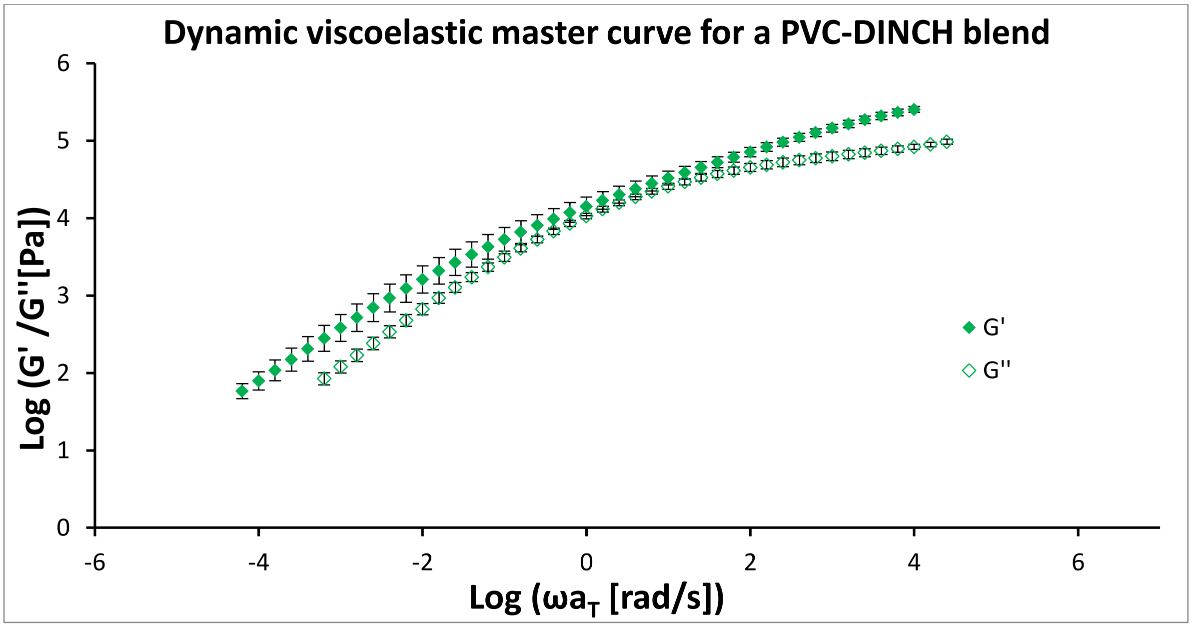

Figure 7: Dynamic viscoelastic master curves (G', G''), prepared through time-temperature superposition, for a 40 PHR PVC-DINCH blend at T_{ref}= 140 °C. Error bars represent standard deviation, n=3

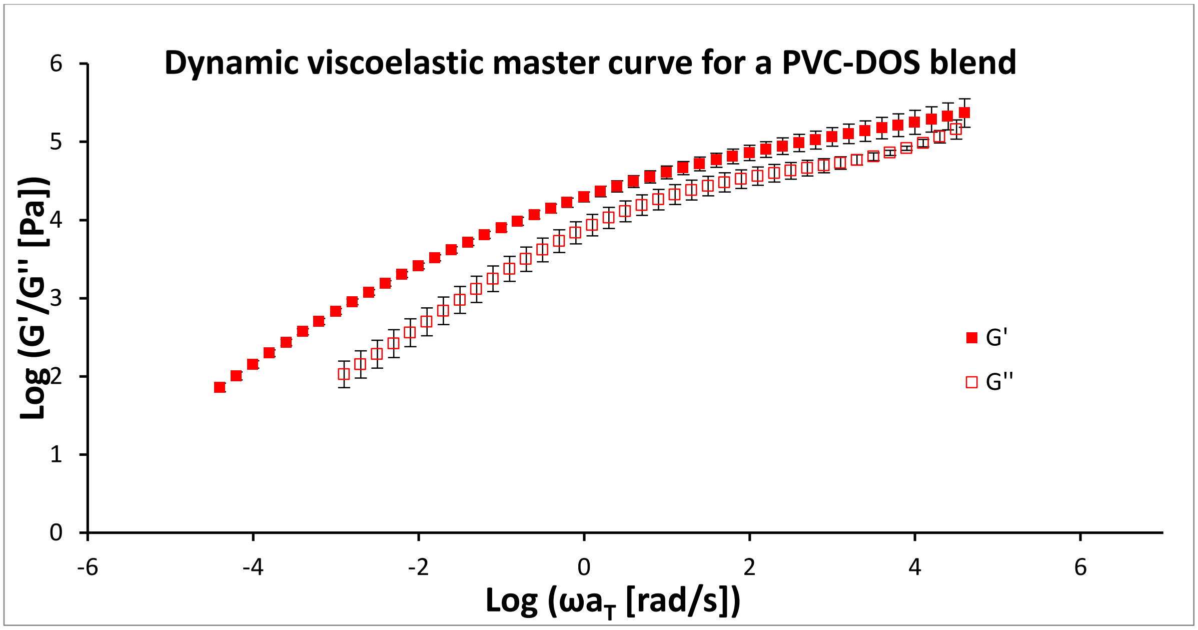

Figure 8: Dynamic viscoelastic master curves (G', G''), prepared through time-temperature superposition, for a 40 PHR PVC-DOS blend at T_{ref}= 140 °C. Error bars represent standard deviation, n=3

The G' and G" master curves for PVC-1,4 BDDB, seen in Figure 9, span a smaller frequency range than the other blends shown in Figures 6-8 due to the fact that degradation of the sample was observed at temperatures greater than 180°C. The isotherms at 190 °C and 200°C were therefore not used to produce the master curves.

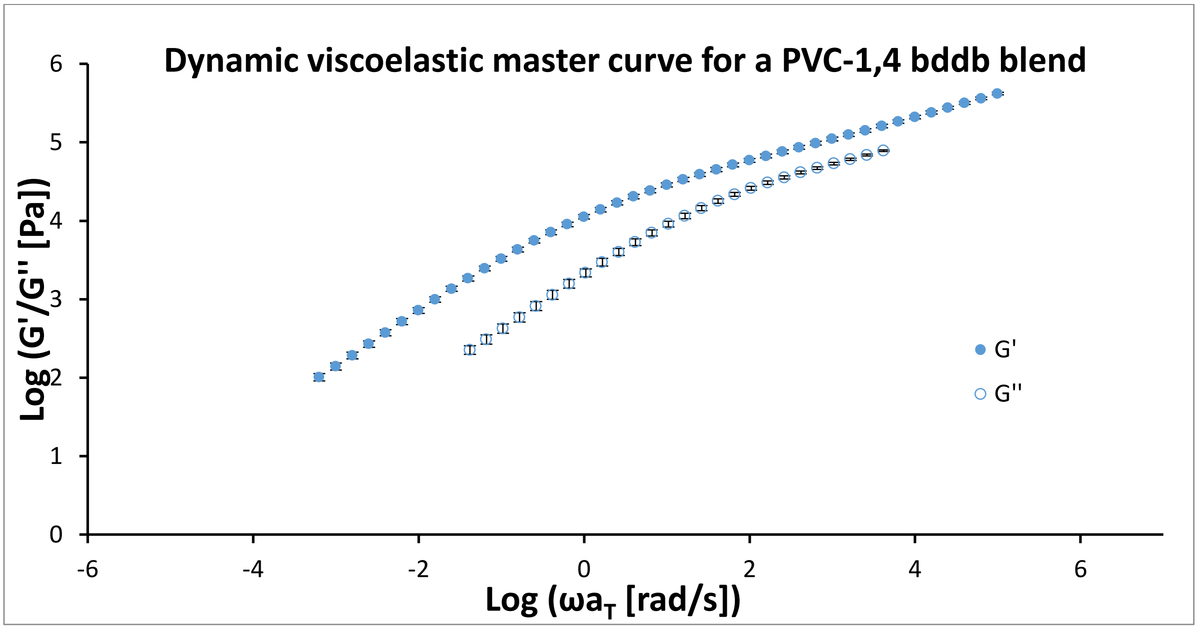

Figure 9: Dynamic viscoelastic master curves (G', G''), prepared through time-temperature superposition, for a 40 PHR PVC-1,4 BDDB blend at T_{ref}= 140 °C. Error bars represent standard deviation, n=2

Figure 10 provides a comparison of the G' master curves for the two green plasticizer blends (DOS and 1,4BDDB) and the two commercial plasticizer blends (DEHP and DINCH). It can be seen that all of the master curves follow the same form. At low frequencies, G' for PVC-DOS is slightly higher than for the commercial plasticizers while G' for PVC-1,4 BDDB is lower.

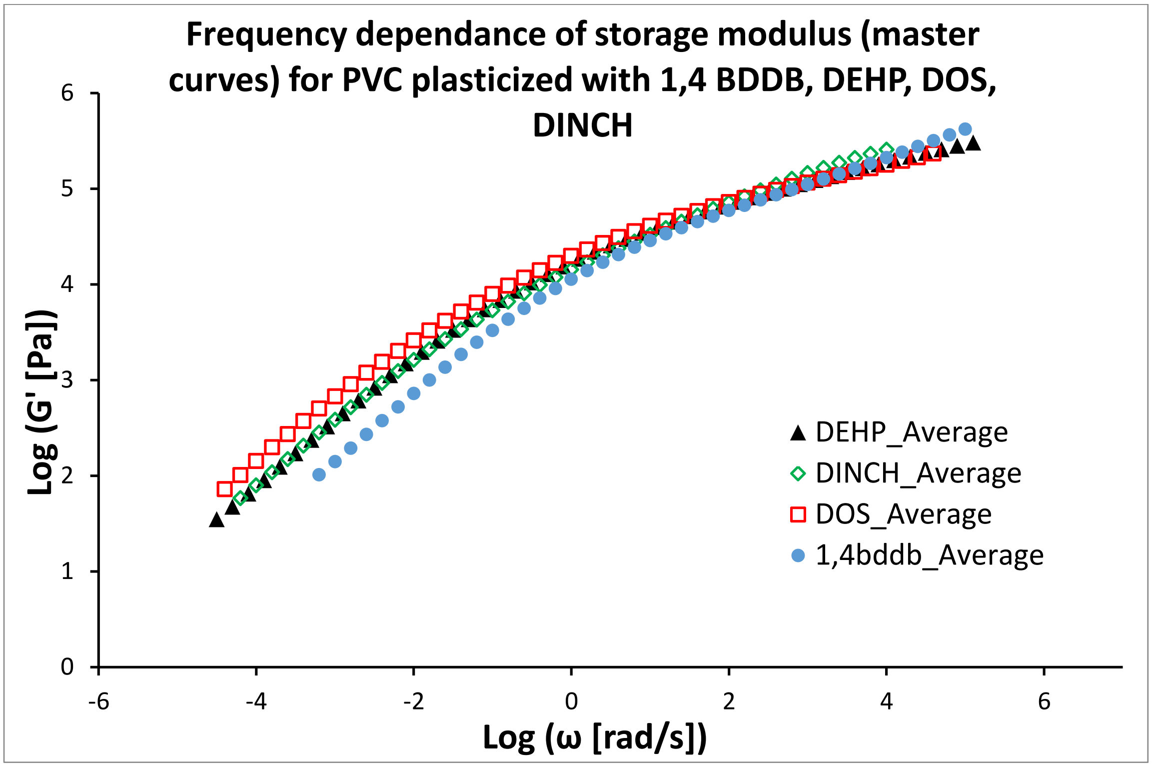

Figure 10: Dynamic viscoelastic master curves (G'), prepared through time-temperature superposition, for green' plasticizers, DOS and 1,4BDDB, compared to commercial plasticizers DEHP and DINCH at T_{ref}= 140°C

Effect of Central Group Chain Length (Dibenzoate Plasticizers)

The generic structure of a dibenzoate plasticizer can be seen in Figure 11. In Figure 12, the viscoelastic master curves of G' are shown for PVC blended with dibenzoate plasticizers synthesized with different central groups. It can be seen that all of the G' curves follow the same form and demonstrate significant overlap along the frequency range of the master curves.

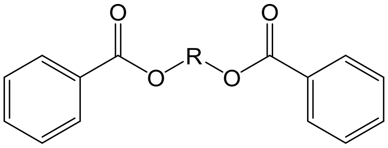

Figure 11: Chemical structure of dibenzoate plasticizer. For 1,3 propanediol dibenzoate (1,3 PDDB) the central group R= C_3H_6, for 1,4 BDDB, R= C_4H_8, for 1,5 PDDB, R= C_5H_{10}, and for 1,6 hexanediol dibenzoate (1,6 HDDB), R= C_6H_{12}

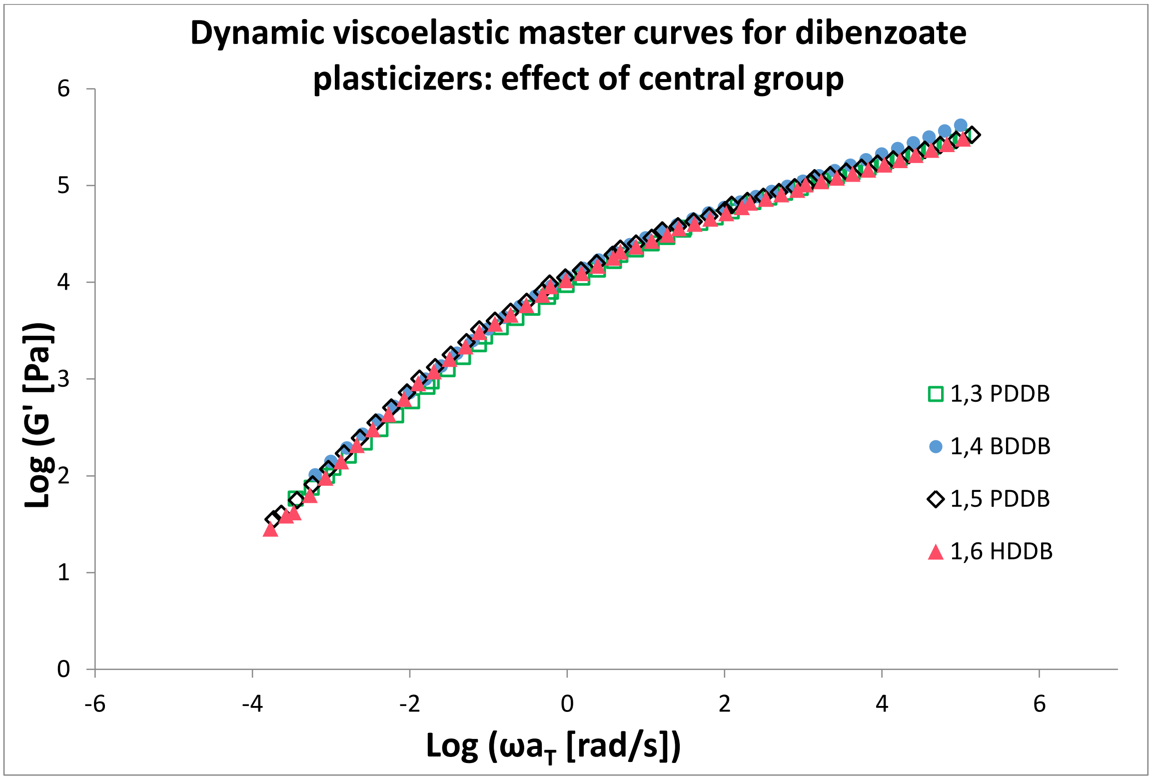

Figure 12: Dynamic viscoelastic master curves (G'), prepared through time-temperature superposition, for PVC blended with dibenzoate plasticizers at T_{ref}= 140 °C

Effect of End Group Chain Length and Branching (Succinate and Maleate Plasticizers)

Figures 13 and 15 show the structure of succinate and maleate plasticizers, respectively. In Figures 14 and 16, G' master curves are shown for PVC blends produced with these plasticizers. Diethyl succinate (DES) and diethyl maleate (DEM) contain the side chain R=$C_2H_{5,}$ di-2-ehtylhexyl succinate (DES) and di-2-ethylhexyl maleate (DEM) contain the side chain R= $CH_3CH(C_2H_5)C_3H_6$, dibutyl succinate (DBS) and dibutyl maleate (DBM) contain the side chain R= C_4H_9, DHS and dihexyl maleate (DHM) contain the side chain R= C_6H_{13}, and DOS and dioctyl maleate (DOM) contain the side chain R= C_8H_{17}.

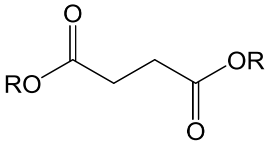

Figure 13: Chemical structure of succinate plasticizer

It can be seen in Figure 14 that PVC blended with succinate plasticizers produce curves that follow the same shape, regardless of chain length or side branch. At high frequencies, the curves demonstrate good overlap for all succinate plasticizer chain lengths, while at lower frequencies, DOS exhibits a slightly higher G' than the rest of the plasticizers, and DHS exhibits a lower G'.

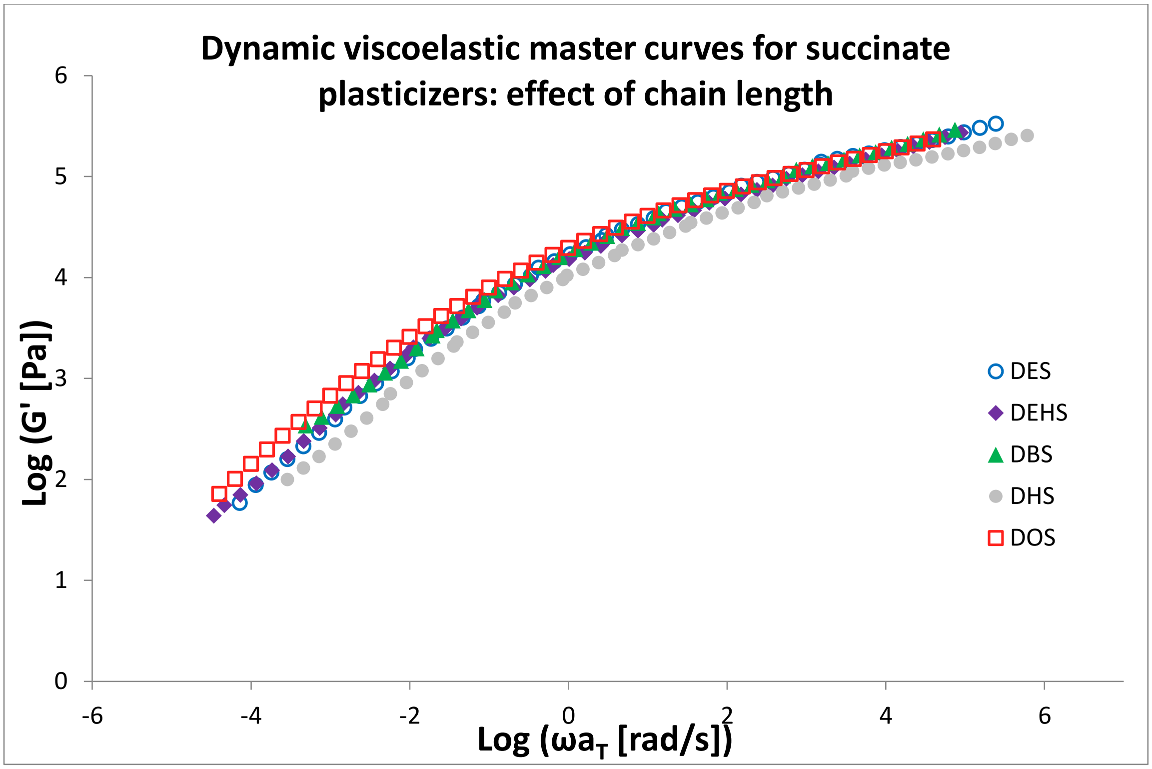

Figure 14: Dynamic viscoelastic master curves (G'), prepared through time-temperature superposition, for PVC blended with dibenzoate plasticizers at T_{ref}= 140 °C

All G' master curves for the PVC-maleate blends follow the same general trend, as seen in Figure 16. PVC-DEM exhibits a significantly higher G' than the other plasticizer blends (unpaired 1-tailed t-test, n ≥3, p <0.05). Addition of the hexyl branch (in DEHM) reduces the G' compared to DEM, a plasticizer of the same chain length, without branching. Similarly, increasing the unbranched chain length also reduces G'. All other blends, except PVC-DEM, have G' curves that overlap significantly. At high frequencies, PVC-DHM has a slightly higher G' than DEHM, DBM, and DOM.

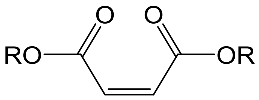

Figure 15: Chemical structure of maleate plasticizer

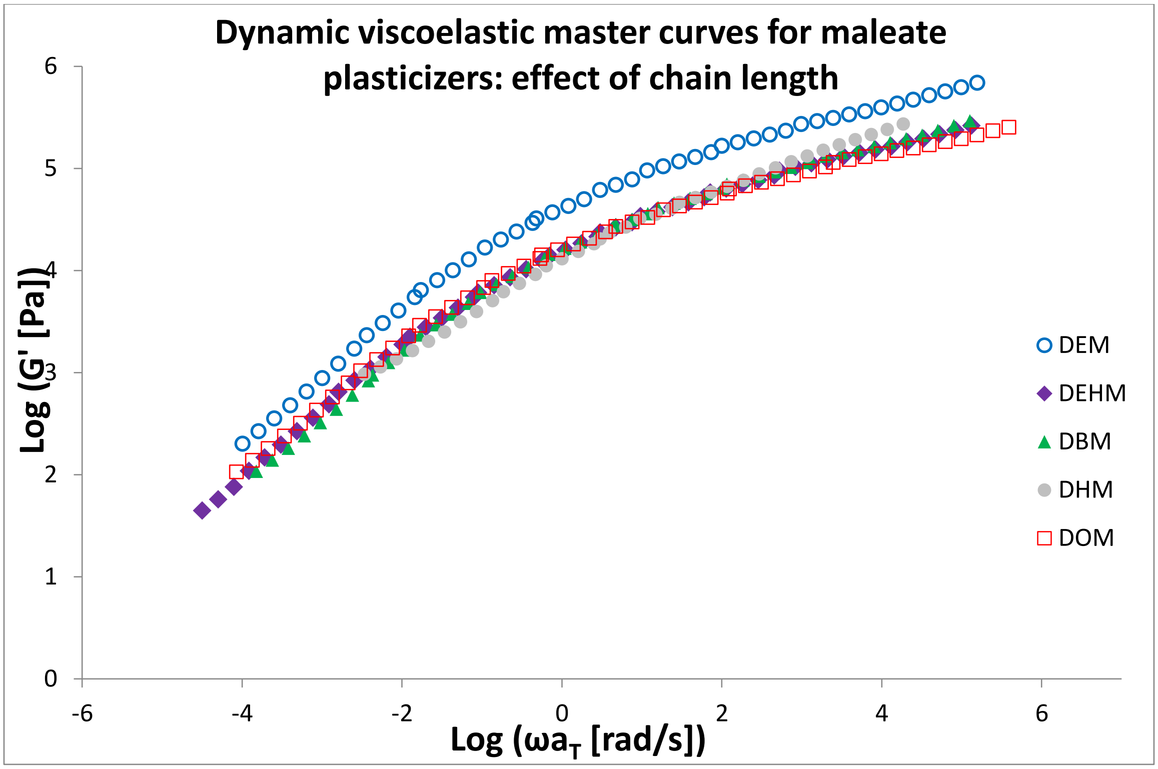

Figure 16: Dynamic viscoelastic master curves (G'), prepared through time-temperature superposition, for PVC blended with maleate plasticizers at T_{ref}= 140 °C

Discrete Relaxation Spectra

In Figure 17, the discrete relaxation times (λ_i), calculated from the experimental G' and G" are shown. It can be seen that the relaxation process for PVC-DEHP consists of seven elementary relaxation modes, while eight relaxation modes were calculated for PVC-DINCH and PVC-DOS, and six modes for PVC-1,4 BDDB.

PVC-DEHP

i	g_i	λ_i
1	$8.2\cdot10^{5}$	$1.3\cdot10^{-5}$
2	$1.1\cdot10^{5}$	$7.7\cdot10^{-5}$
3	$5.4\cdot10^{4}$	$1.6\cdot10^{-2}$
4	$2.2\cdot10^{4}$	0.21
5	$6.4\cdot10^{3}$	2.5
6	$5.6\cdot10^{2}$	39
7	$4.7\cdot10^{2}$	$4.8\cdot10^{3}$

PVC- DOS

i	g_i	λ_i
1	$7.0\cdot10^{5}$	$6.6\cdot10^{-6}$
2	$8.8\cdot10^{4}$	$1.8\cdot10^{-4}$
3	$6.2\cdot10^{4}$	$2.4\cdot10^{-3}$
4	$3.7\cdot10^{4}$	$2.3\cdot10^{-2}$
5	$2.1\cdot10^{4}$	0.16
6	$8.3\cdot10^{3}$	0.99
7	$2.8\cdot10^{3}$	8.2
8	$8.6\cdot10^{2}$	$3.8\cdot10^{3}$

PVC-DINCH

i	g_i	λ_i
1	$3.8\cdot10^{5}$	$2.1\cdot10^{-5}$
2	$1.1\cdot10^{5}$	$7.5\cdot10^{-4}$
3	$6.5\cdot10^{4}$	$1.0\cdot10^{-2}$
4	$3.0\cdot10^{4}$	0.11
5	$1.2\cdot10^{4}$	1.1
6	$3.9\cdot10^{3}$	9.5
7	$4.3\cdot10^{2}$	$1.1\cdot10^{2}$
8	$4.0\cdot10^{2}$	7624.1

PVC-1,4 BDDB

i	g_i	λ_i
1	$6.6\cdot10^{5}$	$5.2\cdot10^{-5}$
2	$8.9\cdot10^{4}$	$2.3\cdot10^{-3}$
3	$3.7\cdot10^{4}$	$3.8\cdot10^{-2}$
4	$1.2\cdot10^{4}$	0.41
5	$1.3\cdot10^{3}$	6.1
6	$1.1\cdot10^{3}$	$4.8\cdot10^{-2}$

Figure 17: Discrete relaxation spectra calculated from experimental G' and G'' data for PVC blended with DEHP, DINCH, DOS, 1,4 BDDB

Figures 18-21 provide a comparison of the experimentally determined frequency dependence of G' and G" to the fitted values determined by the model used to calculate the discrete relaxation spectrum. It can be seen that for all PVC-plasticizer blends the experimental G" correlates strongly with the G" values found by the model. However, the modelled G' values show a strong fit at high frequencies but fail at the lower and middle range of the frequency scale. This trend can be seen for all four plasticizer blends.

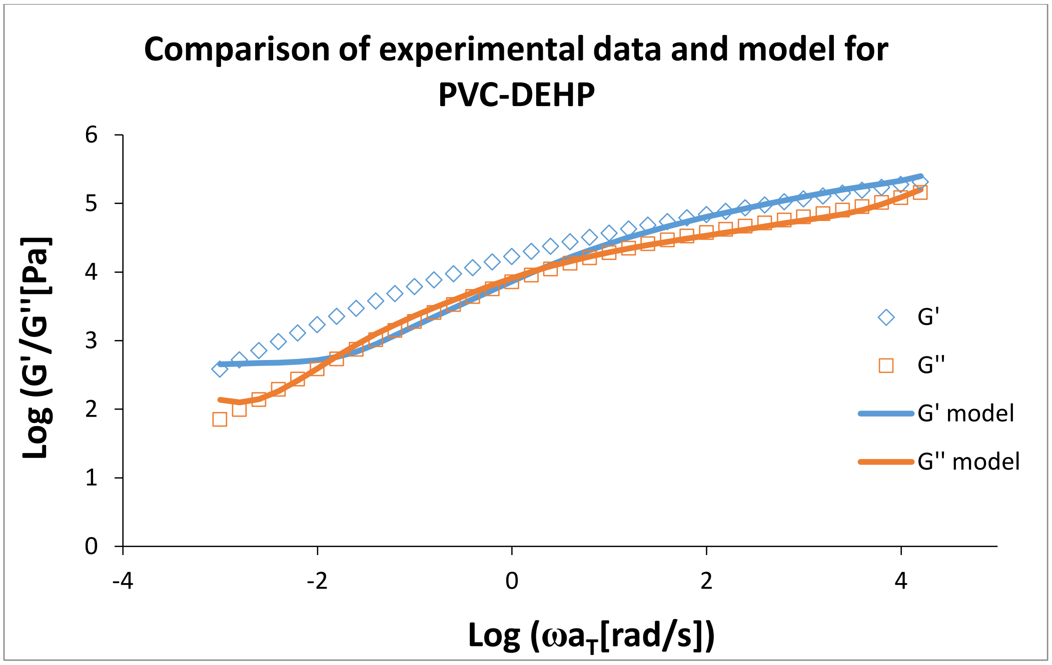

Figure 18: Experimental G' and G'' compared to predicted G' and G'' for PVC-DEHP

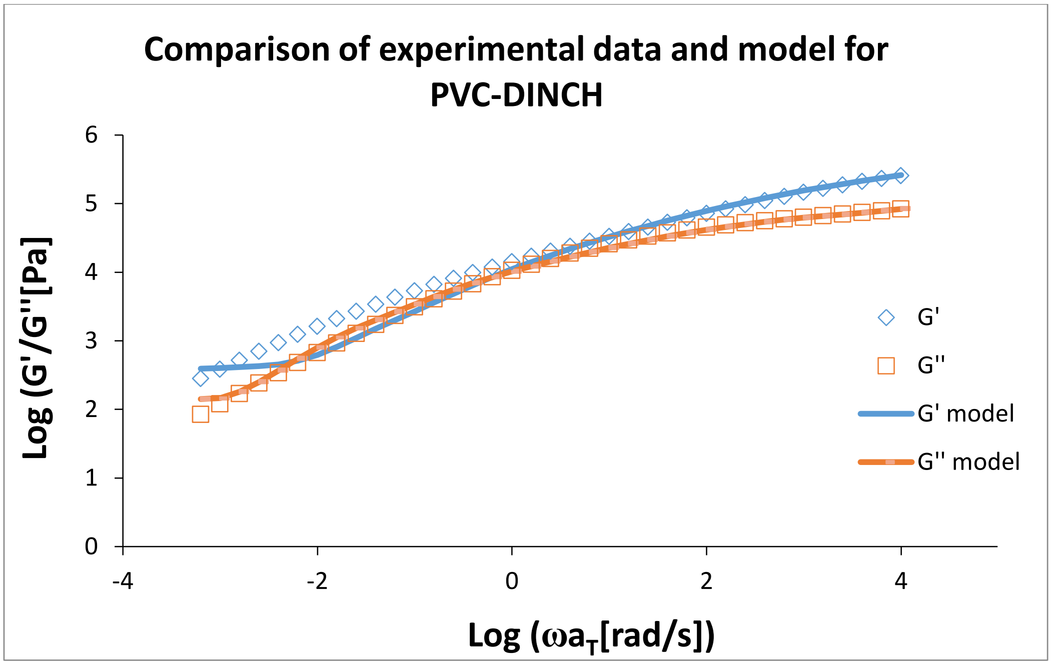

Figure 19: Experimental G' and G'' compared to predicted G' and G'' for PVC-DINCH

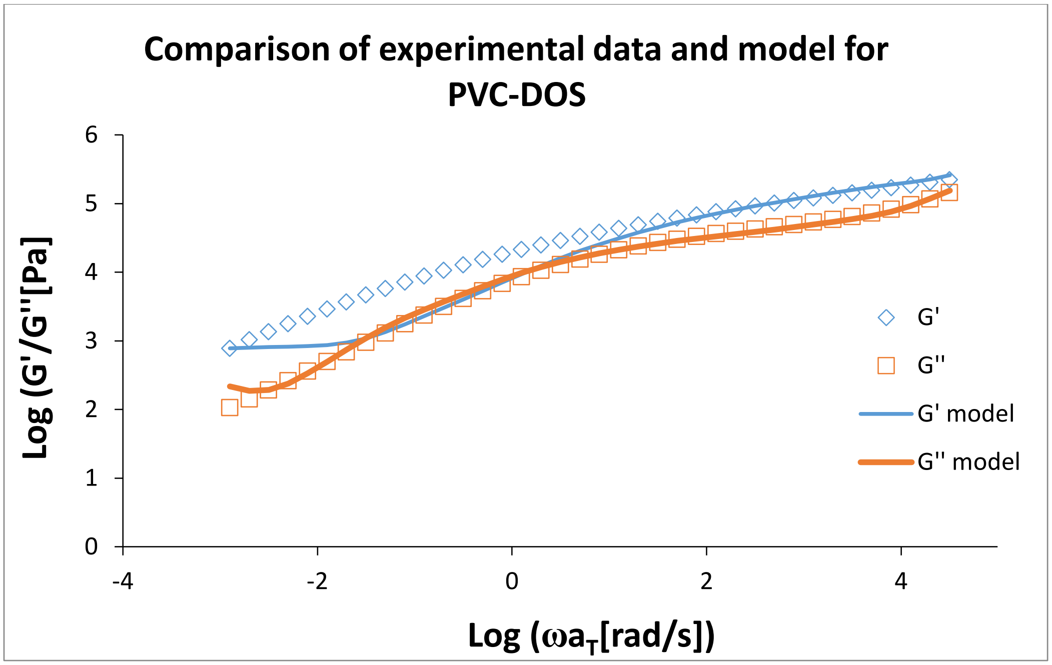

Figure 20: Experimental G' and G'' compared to predicted G' and G'' for PVC-DOS

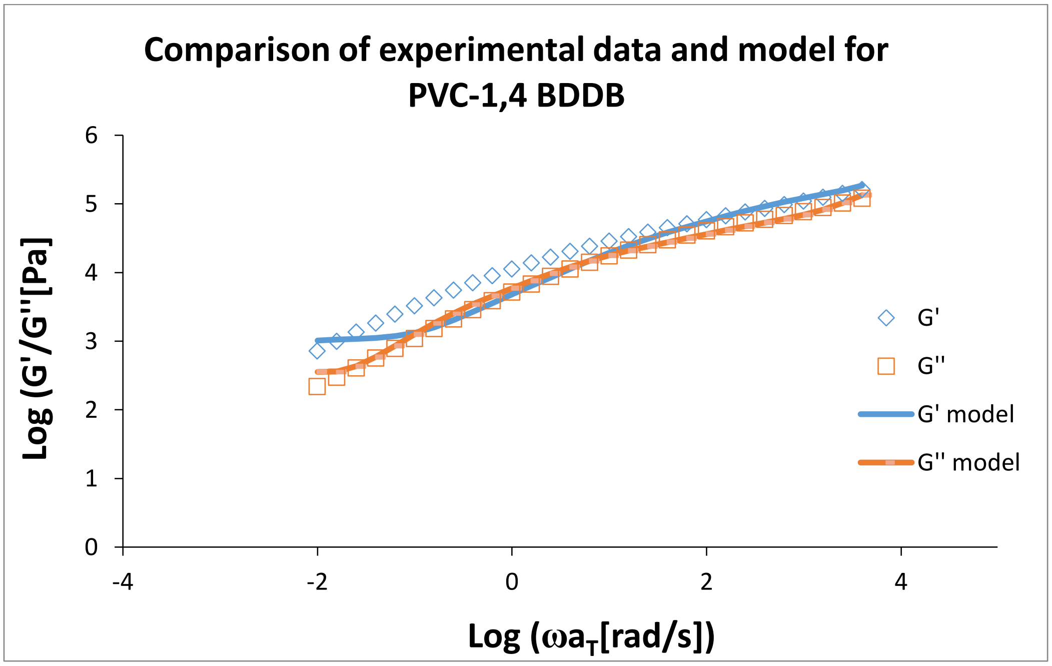

Figure 21: Experimental G' and G'' compared to predicted G' and G'' for PVC-1,4 BDDB

Discussion

Dynamic Mechanical Analysis

The goal of this study was to characterize the rheological behaviour of PVC plasticized with ‘green’ plasticizers. This was achieved by performing dynamic rheological experiments. These tests show the frequency dependence of the storage modulus, G', and loss modulus, G" of the plasticizer blends.

Effect of Temperature and Frequency

It was shown that both G' and G" exhibit temperature and frequency dependence, which is consistent with previous rheological studies conducted on plasticized PVC systems[24]. Both moduli decrease with increasing temperature, and increase with increasing frequency, as seen in Figures 1 and 2. The viscoelastic response of the material cannot be characterized with either a well-defined plateau region or a well-defined terminal relaxation region. While there is an observed increase in G' and G" with frequency, the frequency dependence is weak and not characteristic of a typical terminal region, where sharp increases in moduli are expected. Conversely, in a well-defined plateau region, it is expected that G' remain constant with changes in frequency, which is also not seen in Figures 1 and 2. Possible explanations for this behaviour are large molecular weight distributions in the PVC-plasticizer blends or possible crosslinking from long chain branching and chain entanglements[18].

Time-Temperature Superposition

The maximum shear rates (estimated from the maximum experimental frequencies by the Cox-Merz Rule, which correlates steady shear viscosity versus shear rate to complex viscosity versus angular frequency[30]) that can be achieved through dynamic rheological experiments are significantly lower than those encountered during polymer processing. In order to assess viscoelastic material response over longer frequency ranges than can be experimentally measured, time-temperature superposition was used.

It can be seen in Figure 3 that time-temperature superposition can be applied successfully to PVC-plasticizer blends, as the shifted isotherms overlap well to create a continuous curve. The frequency of the raw data spans approximately 4 orders of magnitude, as seen in Figures 1 and 2, while the frequency of shifted master curve spans around 10 orders of magnitude, as seen in Figure 3, demonstrating the power of time-temperature superposition in describing viscoelastic behaviour at frequencies that cannot be measured experimentally.

The low frequency range of the data at high temperatures demonstrates the weakest overlap of isotherms. Low frequency response represents the long-term behaviour of the polymer. The long-term behaviour of the PVC-plasticizer blends at high temperatures could be influenced by thermal degradation or plasticizer crosslinking, explaining the poor overlap of the curves in this region compared with the rest of the master curve. Overall, however, the overlap is considerable and therefore we can conclude that time-temperature superposition is a valid technique when applied to PVC-plasticizer blends. This conclusion is supported by the fact that the temperature dependence of the horizontal shift factor, seen in Figure 5, is seen to fit well to an Arrhenius model.

Comparison of 'Green' Plasticizers with Commercial Plasticizers

A main goal of this research was to compare the rheological behaviour of PVC blends produced with our 'green' plasticizers to blends produced with commercial plasticizers. Figures 6-9 show the G' and G" master curves, prepared through time temperature superposition, for PVC blended with two common commercial plasticizers, DEHP and DINCH, and two of the promising 'green' plasticizers synthesized by our group, DOS and 1,4 BDDB. It can be seen that all four PVC-plasticizer blends have G' and G" master curves that follow the same general trend, suggesting a similar viscoelastic response. In all four cases, G' is higher than G" for the whole frequency range of the master curve, and no crossover point is observed. This suggests that the material response is predominantly elastic, as opposed to viscous. It also suggests that the material is in the rubbery region. Likely, experiments were not run at low enough frequencies (corresponding to long time scales) for terminal viscous behaviour to be observed. The minimum frequency was chosen based on considerations of experimental run time, so that the time of one experiment and its corresponding nitrogen usage was within reasonable limits. Furthermore, experiments could not be run at temperatures higher than 200°C, which could then have been shifted to lower frequencies, due to the observed degradation of the samples above this temperature. Degradation was evaluated based on observed sample discoloration (test discs turned yellow then brownish black) and steep increases in moduli. At low frequencies, the slope of the G" curve is seen to increase more steeply than the G' curve, whereas at high frequencies the two slopes appear nearly equal. This shows that as frequency increases (corresponding to shorter time-scales), the viscous response of the material becomes more dominant. This is unusual since short time scales are generally characterized by elastic response, while long time scales are characterized by viscous response. However, crosslinking at low frequencies (long times) could explain this trend, since it would inhibit polymer chain movement and, accordingly, viscous flow[31]. The master curves for the 1,4BDDB blend, seen in Figure 9, are the only ones in which the G" curve never reaches the G' curve. This is likely because the master curves span a smaller frequency range than the other plasticizers, due to the fact that the highest temperature achievable experimentally was 180°C, after which degradation was observed. However, the PVC-1,4 BDDB blend does follow the same general trends in terms of the G' and G" slopes.

A comparison of the G' master curves for all four plasticizer blends is presented in Figure 10. All of the G' curves follow the same shape and extensive overlap can be observed, particularly at high frequencies, suggesting that the rheological performance of the ‘green’ plasticizers is comparable to DEHP and DINCH at the reference temperature of 140°C. At high frequencies, the G' curves for all four plasticizer blends appear nearly identical. At low frequencies, G' for PVC-DOS is slightly higher than that of the commercial plasticizer blends, suggesting that the PVC-DOS blend is slightly stiffer. Conversely, at low frequencies, G' for PVC-1,4 BDDB is slightly lower than for the commercial plasticizer blends, indicating greater flexibility and plasticizing ability. At low frequencies, the slope of the G' curve for 1,4 BDDB is also steeper than the other three plasticizers, which is indicative of terminal viscous behaviour and is in agreement with the lower G' values that were observed.

It can be seen that our ‘green’ plasticizer blends display very similar rheological responses to the two commercial plasticizer blends. The 1,4 BDDB blend, in particular, appears to impart more flexibility to the material, suggesting it has a greater plasticizing ability than the commercial plasticizers.

Effect of Plasticizer Central Group Chain Length (Dibenzoate Plasticizers)

To better describe and characterize our ‘green’ plasticizers, we decided to investigate how changing the structure of the plasticizers would affect the rheology of the blend. It was shown in Figure 12 that changing the central group on the dibenzoate plasticizers had no effect on the rheological properties observed. A visual inspection of the G' curves in Figure 12 shows that all of the curves demonstrate the same frequency dependence. All four curves overlap significantly along the whole frequency range of the master curve, and it can therefore be concluded that G' is not affected by the length of the central alkyl group for dibenzoate plasticizers.

Effect of Plasticizer End Group Chain Length and Branching (Succinate and Maleate plasticizers)

It was hypothesized that increasing the length of the alkyl side chains on the succinate and maleate plasticizers would result in these longer chains creating more separation between the PVC molecules, allowing for more overall movement of the chains.

Of the five succinate plasticizer blends compared, chain length was not found to have an effect on the rheology of the materials. The G' curves for all of the plasticizer blends, seen in Figure 14, show similar frequency dependences. G' for the PVC-DOS blend is slightly higher than the other PVC-plasticizer blends at low frequencies, while G' for the PVC-DHS blend is slightly lower. However, these small differences are within the range of experimental error, and no trend based on chain length can be seen.

Of the five maleate plasticizer blends, only PVC-DEM was found to have a G' curve that was significantly greater than the other plasticizer blends (unpaired 1-tailed t-test, $n \geq 3$, $p < 0.05$). It can be seen in Figure 16 that G' for PVC-DEM is higher than for the other plasticizer blends along the whole frequency range of the master curves, suggesting that it is a stiffer material. A possible explanation for this observation is the structure of the maleate central group, which can be seen in Figure 15. The double bond in the maleate central structure prevents rotation about the middle of the molecule and since DEM has the shortest attached side chains of the five maleate plasticizers, the plasticizer structure would be less flexible and have less mobility than the other plasticizers. This could result in poor plasticizing ability compared to the other plasticizers, leading to a higher G'. It was found that DEHM, which has the same chain length as DEM, with an added hexyl branch, has a lower G' than DEM, similar to those of the longer chain plasticizers, when combined with PVC. This could be because the long, flexible hexyl branch allows for greater mobility of the plasticizer molecule compared to the stiff DEM structure. However, the other longer chain plasticizers do not demonstrate a trend of decreasing modulus with increasing chain length. This could be explained by a possible relationship between chain flexibility and chain length where at shorter chain lengths an increase in chain length would correspond to increased flexibility, until a plateau is reached where increasing the chain length no longer has any effect on chain flexibility. The succinate central structure, seen in Figure 13, does not have a double bond and is free to rotate, explaining why DES does not exhibit the same trend as DEM.

Discrete relaxation spectrum

The discrete relaxation spectra were calculated for PVC blended with the 'green' plasticizers DOS and 1,4 BDDB as well as the commercial plasticizers DEHP and DINCH, shown in Figure 17. These values can be used to calculate a variety of viscoelastic material functions. It was found that all of the PVC-plasticizer blends had a similar number of relaxation modes (between 6 and 8), with most of the relaxation time constants (λ_i) for a given mode i, having the same order of magnitude for the different blends. These similarities between the different discrete spectra speak to the similarities of the effect of the 'green' plasticizers and the commercial plasticizers on the rheological properties of PVC.

Experimentally measured G' and G" curves for the four plasticizer blends were compared to G' and G" curves predicted by the discrete relaxation model, to check the validity of the model. It can be seen in Figures 18-21 that the modelled G" values fit the experimental data well for all of the plasticizers. The modelled G' values fit the experimental data well at high frequencies but fail to predict G' behaviour accurately at low frequencies. The G' fit was not improved by increasing N, the number of relaxation modes. This could be because, at low frequencies, the material behaviour does not follow the assumed multi-mode Maxwell model used to calculate the relaxation spectra. At low frequencies, the G' values predicted by the model are lower than the experimentally determined values. Low angular frequencies correspond to long time-scales, which typically allow for greater mobility of the polymer chains and consequently result in a low storage modulus relative to the loss modulus, which is not what is observed in the experimental data (but is what is predicted by the model). Also, the low frequency region of the master curves corresponds to the high temperature isotherms that were shifted through time-temperature superposition to produce the master curve. As previously discussed, effects such as degradation or crosslinking at high temperatures and low frequencies could cause this deviation from the predicted behaviour.

Limitations and Future Work

One of the main limitations of this work was the limited temperature and frequency range over which data was collected. The maximum frequency of the experiments was dictated by instrument limitations, while the minimum frequency was set to achieve reasonable experiment times. In future experiments, it would be beneficial to run longer experiments, to investigate the lower frequency response of the material. The lower temperature limit of the experiments was chosen so that the samples were not too stiff to be deformed by the rheometer while the maximum temperature was set below the point where visible degradation of the samples was observed. While the upper temperature limit cannot be exceeded, the lower temperature range of the experiments can be extended by using a different rheometer configuration. Using rectangular torsion clamps is ideal for stiff, solid samples and could allow for the collection of lower temperature data.

Another limitation of this work is that for the plasticizers used to study the effect of molecular structure, a single batch of PVC blended with the plasticizer was produced and used to collect data. In the future, repeat experiments can be performed for all of the plasticizers to obtain statistical information on batch-to-batch variability. Additionally, the effect of alkyl chain length could be investigated over a longer range of chain lengths, with branching incorporated at the different chain lengths.

Other areas that would be of interest to investigate are the effect of plasticizer concentration on the rheological properties of the material, for the different 'green' plasticizers. As well, the effect of varying the concentration of the other additives in the PVC-plasticizer blend could be of interest, to determine optimum additive amounts. More work can also be done on improving the fit of the discrete relaxation models to the experimental data.

Conclusions

In this work, the rheological behaviour of PVC blended with ‘green’ plasticizers was characterized using dynamic mechanical analysis and discrete relaxation time spectra. Additionally, the behaviour of the ‘green’ plasticizer blends was compared to two commercially available plasticizers, DEHP and DINCH.

It was shown that the frequency range over which the material response was studied could effectively be increased using time-temperature superposition. Furthermore, it was shown that changing the central structure of dibenzoate plasticizers had no effect on their plasticizing ability, as evidence by their similar G' master curves. Similarly, changing the alkyl side chain length of succinate plasticizers had no effect on the G' master curves. PVC blended with DEM, the maleate plasticizer with the shortest alkyl side chain, was found to have a higher G' than the other maleate plasticizer blends, implying that it is stiffer. It is hypothesized that the central structure of the maleate plasticizer, which includes a double bond that inhibits movement, combined with a short ethyl group, causes an inflexible and consequently less effective plasticizer.

The G' and G" viscoelastic master curves for DOS and 1,4 BDDB compared favourably to those of the commercial plasticizers DEHP and DINCH. The ‘green’ plasticizers exhibited similar rheological behaviour to the commercial plasticizers, as seen by the comparable shape of the G' and G" master curves. DOS exhibited marginally higher G' values than its commercial counterparts at low frequencies, while 1,4 BDDB exhibited lower G' values. Based on this, it was concluded that 1,4 BDDB was the better ‘green’ plasticizer, although both plasticizers demonstrated similar behaviour to DEHP and DINCH. The discrete relaxation spectra were also calculated for 1,4 BDDB and DOS as well as for DEHP and DINCH. The ‘green’ plasticizers were found to have a comparable number of relaxation modes and similar time constants to the commercial plasticizers, further proving their effectiveness as plasticizers.

This work has established that the rheological properties of the ‘green’ plasticizers 1,4 BDDB and DOS are comparable to those of commercial plasticizers. The next step in determining whether these ‘green’ plasticizers are suitable for replacement industrially would be a thorough economic analysis. Ultimately though, government policy phasing out or banning phthalate plasticizers will likely need to be the driver for large-scale industrial change. Our ‘green’ plasticizers could provide an appropriate alternative.

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