The object of this study was to investigate the relaxation time ($\lambda_k$) and the viscosity index ($\eta_k$) of a tyre tread compound. The rheological behaviour of the sample was studied using a parallel plate rheometer and the rheological material functions, such as complex shear viscosity ($\eta^*$), elastic shear modulus ($G'$), and viscous shear modulus ($G''$) were measured in frequency sweep test (FST). The study has focused on a method for calculating $\lambda_k$ and the $\eta_k$ using generalized Maxwell model (GMM) over a limited range of frequency and temperature. Time sweep test, stress sweep test and frequency sweep test were carried out using a parallel plate rheometer. The stable zone (or steady state region) which is suitable for measuring the rheological material functions was obtained from time sweep test results at various temperatures and frequencies. Stress sweep test was then carried out to determine linear viscoelastic zone of the compound at a given temperature and frequency. The critical stress, which determines the linear-nonlinear transition point, was obtained from stress sweep test results at each temperature and frequency. The complex shear viscosity ($\eta^*$), elastic shear modulus ($G'$), and viscous shear modulus ($G''$) were measured in frequency sweep test and the relaxation time was then calculated. The results showed that the rheological behaviour of the compound followed the GMM. The relaxation time was also found to be a decreasing function of both temperature and frequency.

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ABSTRACT

Key Words: tyre tread compound; parallel plate rheometer; generalized Maxwell model; linear viscoelastic; relaxation time.

INTRODUCTION

In the tyre industry, extrusion is a major operation in the manufacturing of tyre tread compounds [1]. A rubber compound is usually a mixture of elastomers, filler, plasticizer, lubricant, processing aid, antioxidant, curing systems and some other additives. Different ingredients in a rubber compound may affect the flow behaviour of compound. Compound preparation or mixing is carried out in an internal mixer and a two-roll mill. This operation leads to a heterogeneous and complex mater-
rrial, with strong flow anisotropy, severe shear thinning and non-linear viscoelastic behaviour. Elastomer-additives interactions can be studied by some methods either direct methods such as a solid nuclear magnetic resonance (NMR), or indirect methods such as a bond rubber assessment. Certain rheological techniques are also interesting because they provide information that can be considered with respect to processing conditions. Studies show that the rheological material functions for rubber compounds have still not been completely resolved [2-9]. This is due to the fact that the complex and non-linear deformation behaviour of viscoelastic materials cannot be easily described. Also, the properties of the end product in tyre manufacturing are greatly affected by the processing conditions (e.g., temperature and/or pressure), which are determined by the rheological characteristics of the rubber compound [10]. Therefore, the flow properties of a filled system such as a rubber compound are influenced by the rheological behaviour of the rubber matrix, particle characteristics, dispersion state and the interaction between particles and rubber matrix [11].

There are several theoretical models, which have been used to describe linear viscoelastic data. To describe the viscoelastic response of a rubber compound, Drozdov [12] modelled it as a composite medium, where regions with low concentrations of junctions are randomly distributed in the bulk material. Strong interactions between filler and polymer have been recognized as the main source of the reinforcing effect. The interactions between the components and the chain mobility of rubber also affect the rheology properties of the compound such as relaxation time[13]. The viscoelastic parameters generally vary over several orders of magnitude. To minimize this effect, investigations have been carried out in different limited times, stresses and frequencies [14-17].

Many methods for studying the rheological behaviour have been developed using torsional dynamic rheometer [18-23]. A two-parallel plate rheometer is generally used to study the plateau region or stability zone, where all the rheological material functions remain constant [24-25]. Also the linearity zone, where the rheological behaviour remains unchanged with stress changes, should be determined [10]. After recognition of the stable zone by time sweep test and the linearity zone by stress sweep test were carried out in order to measure particular rheological material functions and the relaxation times and viscosity indexes were then calculated.

The aim of this study was to find a method for calculating the $\lambda_k$ and $\eta_k$ of tyre tread compounds at a limited range of frequency and different temperatures using a parallel plate rheometer. For this purpose, GMM was used to calculate the relaxation time ($\lambda_k$) and viscosity index ($\eta_k$) on a limited range of frequency in the isothermal condition. It was found that the rheological behaviour of sample was fitted on GMM and the $\lambda_k$ and $\eta_k$ were decreased with increasing temperature and frequency.

In our study, $\lambda_k$ and $\eta_k$ in GMM at a given range of frequencies, have been calculated for the first time, so the results would be used for further calculations on simulation of an extrusion process of a tyre tread.

**EXPERIMENTAL**

**Materials and Sample Preparation**

The materials used in this study were based on model passenger tyre tread compound without curing system (or master). The compound included two types of styrene-butadiene rubber (SBR1500 and SBR1712, produced by Bandar Imam, Petrochemical Co. (BIPC), Iran), as a rubber base, carbon black (N-375, Doodeh Pars Co., Iran) as a reinforcement, aromatic oil (Behran Oil Co., Iran) as softener, ZnO (Rangineh Pars Co., Iran) as an activator, $N$-1,3-dimethylbutyl-$N'$-phenyl-$p$-phenylenediamine (6PPD, Vulkanox4020, Bayer Co., Germany) and 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ, Vulkanox HS, Bayer Co., Germany) as antioxidant and antiozonant, stearic acid (Unichema International Co., Malaysia) as an activator, microwax (Unichema International Co., Malaysia) as a processing aid, rosin and tackifier resin (Schenectady Co., Europe) as a tackifying agent.

The rubber compound was prepared according to the formulation described in Table 1. SBR1500, SBR1712, carbon black, oil, and other additives were mixed in a one-L laboratory banbury mixer (Farrel model) for 15 min as master compound. The master compound was then sheeted off on a two-roller mill. The sheet was stored for 24 h at room temperature to relax the mixing shear stresses. Then, the compound was
cold pressed to form disk-shape specimens, with the thickness of about 3 mm. The specimens were stored again for 24 h at room temperature to relax shaping shear stresses and then the rheological examinations were carried out on the specimens.

Rheological Studies
Rheological properties of the sample were determined using a torsional dynamic instrument (SR5000 from TA Instruments). This instrument is capable to test highly viscous materials and includes two parallel plates with the lower plate, which oscillates in torsion at controlled stresses and frequencies at isothermal conditions. The torque measuring system is fixed on the upper plate and it is calibrated with a torsion spring. The temperature is controlled carefully within the resolution to the nearest 0.1 C. The instrument is fully monitored by a computer with the capability of combining pre-programmed test sequences in any order.

A disk shape sample of uncured tyre tread compound was placed in the gap between the parallel plates; the lower plate was oscillated sinusoidally in torsion after running the test. For finding the stable zone in time sweep test, all of the rheometry conditions such as frequency, shear stress and temperature were kept constant and the stable zones were found at various conditions. In determining the linear viscoelastic zone from stress sweep test, the frequency was kept constant and the stress was varied between 100 and 15000 Pa. The $G'$, $G''$, and $\eta^*$ were measured as functions of the stress. Therefore, the critical stress or linear viscoelastic zone for each frequency and temperature was determined. Finally the rheological material functions were measured by frequency sweep test, in which the frequency scanned from 0.01 to 10 Hz.

In the beginning of the test, recorder of the rheometer showed that the output signal was also sinusoidal but out-of-phase by an angle $\delta$, depending on viscous character of the material. This is expressed mathematically with the following equation:

$$\eta^* = (\eta^* - \eta^*)^{1/2} = \left(\frac{G''}{\omega^*} + \frac{G'}{\omega^*}\right)^{1/2}$$

where, $\omega$ is the frequency, $G'$ is the in-phase or elastic modulus, and $G''$ is the out-of-phase or viscous or loss modulus.

RESULTS AND DISCUSSION
Time Sweep Test
The purpose of time sweep test (TST) was to obtain the stable zone at a given condition. The stable zone was determined using various temperatures, frequencies and stresses. In time sweep test, storage modulus, loss modulus and complex viscosity are studied at constant temperature, frequency and stress (or strain) and the material functions such as moduli or viscosity were plotted against time. In this test, it was observed that, at a constant stress, the extension of stable plateau was reduced as the frequency was increased, and the same result was observed when stress value was increased and the frequency was kept constant.

Figures 1-3 show the unstability at the start of the test because the interactions between components of the compound is damaged under shear force and deviation in this region can be observed. The same deviation was repeated after a stable period of time because of applying heat and shear forces which are probably due to a slight cross-linking or some interactions of compound ingredients with time. It is generally known when a rubber compound is deformed sinusoidally, within a few cycles of start-up, it shows a deviation in

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>phr*</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR1500</td>
<td>45.0</td>
</tr>
<tr>
<td>SBR1712</td>
<td>55.0</td>
</tr>
<tr>
<td>N-375</td>
<td>60.0</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.0</td>
</tr>
<tr>
<td>Aromatic oil</td>
<td>3.0</td>
</tr>
<tr>
<td>Rosin</td>
<td>4.0</td>
</tr>
<tr>
<td>Tackifier resin</td>
<td>2.0</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2.0</td>
</tr>
<tr>
<td>Micro wax</td>
<td>1.0</td>
</tr>
<tr>
<td>6PPD</td>
<td>1.5</td>
</tr>
<tr>
<td>TMQ</td>
<td>1.0</td>
</tr>
</tbody>
</table>

(*) phr: per hundred rubber

Table 1. Tyre tread compound.
rheological behaviour and unstability because of thermal diffusion and heterogeneity in compound. The time sweep test was done at 80°C, 100°C, and 120°C. In each temperature the stress was applied at three controlled levels of 1000, 5000, and 10000 Pa. Each test was repeated at three frequencies of 0.628, 6.28, and 62.8 rad/s (or 0.1, 1, 10 Hz).

As shown in Figure 1, with increasing the temperature, the moduli (the results illustrate G' and G'') are decreased and the stable zone is also determined.

Figure 2 shows that G' decreases as the controlled stress is increased. Higher constant stress results in higher strain and, therefore, causes the morphology damaging to occur in earlier stages. Thus, with increasing the constant stress the stable zone is decreased.

Figure 3 shows that G' increases with the increase of frequency but the stable zone is decreased.

Figures 1, 2, and 3 illustrate the time stability or safety time for rheological studying at various conditions. Results obtained from time sweep test show that the plateau are obtained in about 500 to 2500 s. This time period is called stable zone and at this period no changes in rheological material functions is observed and, therefore, it is suitable for studying the rheological behaviour of the samples.

Stress Sweep Test
In the next step, the linear zone was found. As the stress sweep test (SST) is started, the stress (or strain in strain sweep test) is increased and it reaches the critical stress, in which, a linear behaviour is changed to a non-linear behaviour. This behaviour is believed to reflect the nature of polymer and specially the rubber compounds studied. Before this critical point the rheological parameters are constant, but above that, non-linear zone is found which is due to damaging of rubber-additives morphology. It is generally known, that finding the linear viscoelastic zone for rubber compounds is very difficult because of the complex interactions between the components of rubber and it is related to many conditions such as temperature, frequency and stress (or strain). Although in some literature strain sweep test has been used for finding the linear viscoelastic zone for polymer melts [17-21], but due to
stronger slip effect in rubber compounds than other polymers stress sweep test is found to be more effective. It is clear, that the strain increases as stress increases and large damaging strains are occurred. Therefore, the rheological material functions reached a non-linear region.

As it can be seen in Figure 4 the length of linear plateau decreases as the frequency increases and the critical stress or linear viscoelastic zone is shifted towards lower stresses.

Figure 5 shows the relation between critical stress and temperature. As shown in this figure the critical stress decreases with increasing temperature. The tests were continued and Table 2 shows the critical stresses obtained from stress sweep test at different temperatures and frequencies.

**Frequency Sweep Test**

Frequency sweep test is the last test for finding out the rheological material functions. Considering the stable zone and linear viscoelastic zone, which were obtained from the time and stress sweep test, respectively the frequency sweep test was run. Figures 6-8 show master curves of rheological material functions of the sample at different temperatures. It is very important that the test is done for each frequency domain regarding the related critical stress. Now, there would be a question, that why there is a need to find the relation between critical stress (or strain) and frequency? The answer is that in the high shear rates, the sensitivity of the rheological material functions is decreased.

As shown in these Figures, $\eta^*$ is decreased and $G'$ and $G''$ are increased with increasing the frequency or shear rate. The results of these tests for various temperatures, frequencies, and constant stresses (almost near the critical stresses) were obtained and superimposed in the master curves.

**Relaxation Times Distribution**

Boltzmann superposition principle describing linear viscoelastic behaviour may be given as:

$$\tau(t) = \int_{-\infty}^{t} G(t-t') \gamma(t') \, dt'$$

(2)

where, $G(t)$ is the linear relaxation modulus and $\gamma$ is the shear rate.

The most popular approach to describe the behaviour of polymer melts in linear viscoelastic experiments is a generalized Maxwell model. The function used in

**Table 2. Critical stress at various frequencies and temperatures.**

<table>
<thead>
<tr>
<th>Frequency(rad/s)</th>
<th>0.628</th>
<th>6.28</th>
<th>62.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature(°C)</td>
<td>$\sigma_1^c$</td>
<td>$\sigma_2^c$</td>
<td>$\sigma_3^c$</td>
</tr>
<tr>
<td>80</td>
<td>14196</td>
<td>11155</td>
<td>5912</td>
</tr>
<tr>
<td>100</td>
<td>10471</td>
<td>7943</td>
<td>2238</td>
</tr>
<tr>
<td>120</td>
<td>7943</td>
<td>4467</td>
<td>-</td>
</tr>
</tbody>
</table>
this model is:

\[ G(t - t') = \sum G_k \exp[-(t - t')/\lambda_k] \]  

(3)

where, \( G_k \) is the relaxation modulus, \( \lambda_k \) is the relaxation time, and \( k \) is the discrete experimental data.

From oscillatory shear experiments, the model parameters \( (G_k, \eta_k, \lambda_k) \) can be determined by using the following equations [15]:

\[ G'(\omega) = \sum G_k \frac{\omega^2 \lambda_k^2}{1 + \omega^2 \lambda_k^2} \]  

(4)

\[ G''(\omega) = \sum G_k \frac{\omega \lambda_k^2}{1 + \omega^2 \lambda_k^2} \]  

(5)

\[ \eta'(\omega) = \sum \frac{\eta_k}{1 + \omega^2 \lambda_k^2} \]  

(6)

\[ \frac{\eta''(\omega)}{\omega} = \sum \frac{\eta_k \lambda_k^2}{1 + \omega^2 \lambda_k^2} \]  

(7)

In the expressions given \( \omega \) refers to the experimental frequency.

In this study the linear least-square method was used to obtain the relaxation time and the viscosity index. For five sets of experimental range of frequencies, the model parameters \( (\eta_k, \lambda_k) \) were calculated using the eqn (6) and the experimental sets of data.

For this purpose, the eqn (6) was re-written as follows:

\[ \frac{1}{\eta'_(\omega)} = \frac{1}{\eta_K} + \frac{\lambda^2 K}{\eta_K} \omega^2 \]  

(8)

This equation can be written as:

\[ Y = A + BX \]  

(9)

where,

\[ Y = \frac{1}{\eta'_(\omega)}, X = \omega^2, A = \frac{1}{\eta_k}, B = \frac{\lambda^2_k}{\eta_k} \]

Thus, relation between \( 1/\eta'_(\omega) \) and \( \omega^2 \) can be found with splitting into various limited ranges of frequencies and \( 1/\eta'_(\omega) \) versus \( \omega^2 \) at each temperature can be plotted. The values of parameters which were obtained using this method are in a good agreement with the experimental \( \eta'_(\omega) \) data. The results are summarized in Table 3. After calculating the A and B in eqn (9) the
Table 3. The values of A and B in Y = A + BX of eqn (9) and R squared after linear interpolation.

<table>
<thead>
<tr>
<th>Temperature (C)</th>
<th>ω (rad/s)</th>
<th>A</th>
<th>B</th>
<th>R²</th>
<th>A</th>
<th>B</th>
<th>R²</th>
<th>A</th>
<th>B</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>80</td>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td></td>
<td></td>
<td>120</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0628-0.314</td>
<td>3 × 10⁻⁷</td>
<td>4 × 10⁻⁶</td>
<td>0.98</td>
<td></td>
<td>15 × 10⁻⁶</td>
<td>17 × 10⁻⁶</td>
<td>0.97</td>
<td>2 × 10⁻⁶</td>
<td>2 × 10⁻⁵</td>
<td>0.97</td>
</tr>
<tr>
<td>0.314-8.16</td>
<td>3 × 10⁻⁶</td>
<td>9 × 10⁻⁸</td>
<td>0.98</td>
<td></td>
<td>8 × 10⁻⁸</td>
<td>2 × 10⁻⁷</td>
<td>0.98</td>
<td>1 × 10⁻⁵</td>
<td>2 × 10⁻⁷</td>
<td>0.96</td>
</tr>
<tr>
<td>8.16-18.84</td>
<td>3 × 10⁻⁷</td>
<td>3 × 10⁻⁸</td>
<td>0.97</td>
<td></td>
<td>1 × 10⁻⁸</td>
<td>27 × 10⁻⁹</td>
<td>0.96</td>
<td>2 × 10⁻⁵</td>
<td>4 × 10⁻⁸</td>
<td>0.96</td>
</tr>
<tr>
<td>18.84-37.68</td>
<td>3 × 10⁻⁸</td>
<td>2 × 10⁻⁸</td>
<td>0.98</td>
<td></td>
<td>15 × 10⁻⁸</td>
<td>2 × 10⁻⁸</td>
<td>0.98</td>
<td>____</td>
<td>____</td>
<td>____</td>
</tr>
<tr>
<td>37.68-62.8</td>
<td>3 × 10⁻⁸</td>
<td>9 × 10⁻⁸</td>
<td>0.99</td>
<td></td>
<td>3 × 10⁻⁸</td>
<td>15 × 10⁻⁹</td>
<td>0.98</td>
<td>4 × 10⁻⁸</td>
<td>4 × 10⁻⁸</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Table 4. The η_k and λ_k in Maxwell model of eqn (8) at three different temperatures and limited range frequencies for tyre tread compound.

<table>
<thead>
<tr>
<th>Temperature (C)</th>
<th>ω (rad/s)</th>
<th>η_k</th>
<th>λ_k</th>
<th>η_k</th>
<th>λ_k</th>
<th>η_k</th>
<th>λ_k</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>80</td>
<td>100</td>
<td>120</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0628-0.314</td>
<td>3.33 × 10⁶</td>
<td>6.67 × 10⁰</td>
<td>5.00 × 10⁵</td>
<td>3.6514 × 10⁰</td>
<td>3.3665 × 10⁰</td>
<td>3.1622 × 10⁰</td>
<td></td>
</tr>
<tr>
<td>0.314-8.16</td>
<td>3.33 × 10⁵</td>
<td>1.25 × 10¹</td>
<td>1.00 × 10⁵</td>
<td>1.7320 × 10⁻¹</td>
<td>1.5811 × 10⁻¹</td>
<td>1.4142 × 10⁻¹</td>
<td></td>
</tr>
<tr>
<td>8.16-18.84</td>
<td>1.43 × 10⁵</td>
<td>5.00 × 10⁴</td>
<td>5.00 × 10⁴</td>
<td>6.5465 × 10⁻²</td>
<td>5.1961 × 10⁻²</td>
<td>4.4721 × 10⁻²</td>
<td></td>
</tr>
<tr>
<td>18.84-37.68</td>
<td>1.00 × 10⁵</td>
<td>3.33 × 10²</td>
<td>____</td>
<td>4.4721 × 10⁻²</td>
<td>2.2360 × 10⁻²</td>
<td>____</td>
<td></td>
</tr>
<tr>
<td>37.68-62.8</td>
<td>5.00 × 10⁴</td>
<td>3.34 × 10²</td>
<td>2.50 × 10⁴</td>
<td>2.1213 × 10⁻²</td>
<td>____</td>
<td>2.2360 × 10⁻²</td>
<td></td>
</tr>
</tbody>
</table>

parameters of GMM are then obtained.

Table 4 shows the GMM parameters which were determined from Table 3 at temperatures of 80, 100, and 120 °C.

CONCLUSION

Rheological properties of a tyre tread compound, which is a complex rubber compound were characterized by oscillatory shear tests using parallel plate rheometer.

Results obtained from time sweep test showed that the plateau time region depends not only on frequency but also on stress values. The results showed that the stable zone decreased with increasing frequency and stress values. In this test some variations in rheological material functions were observed. This behaviour is related to the nature of the sample and the thermal heterogeneity of the rubber compound at the beginning of the test. After the stable time partial cross-linking and interaction between ingredients occurred and the deviation was noticed again.

The linear viscoelastic zone from stress sweep test was determined. The tyre tread compound showed linear viscoelastic behaviour up to a critical stress. It was observed that the critical stress or the linear viscoelastic plateau was related to the frequency and temperature. The critical stress was shifted to lower stresses with increasing temperature and frequency.

After finding the stable zone and the LVE zone, the frequency sweep test was done and the rheological parameter functions were then determined.

A method based on the generalized Maxwell model was used to calculate η_k and λ_k. The results showed that the η_k, a characteristic of viscosity, was decreased with increasing temperature and frequency due to the decrease in viscosity. As λ_k, the relaxation time, was decreased with the increase of temperature and frequency, it can be concluded that these material functions are related to the rubber chain mobility.

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REFERENCES


