Chapter 5
Dynamic Mechanical and Thermal Properties

Abstract
The dynamic mechanical properties of macro and micro fibers of oil palm reinforced natural rubber (NR) and nitrile rubber (NBR) composites were investigated as a function of fiber content, temperature, treatment and frequency. By the incorporation of macro fiber in natural rubber and nitrile rubber, the storage modulus (E’) and loss modulus values increases while damping factor (\(\tan \delta\)) decreases. As the fiber content increases the damping nature of the composite decreases due to the increased stiffness imparted by the natural fibers. By steam explosion method (STEX) micro fibers are separated from oil palm fibers. These fibers were undergone treatments like mercerization, benzoylation and silane treatment. Resorcinol-hexamethylene tetramine-hydrated silica (HRH) is also used as bonding agent to increase the fiber/matrix adhesion. The storage modulus values of untreated and treated micro fiber reinforced composites were higher than that of macro fiber reinforced composites. The \(T_g\) value obtained for this micro fibril reinforced composites shows slightly higher values than that of macro fiber reinforced composites. Activation energy for the relaxation processes in different composites was calculated. Morphological studies using scanning electron microscopy (SEM) of tensile fracture surfaces of treated and untreated composites indicated better fiber/matrix adhesion in the case of treated micro fibril reinforced composites. Finally attempts were made to correlate the experimental dynamic properties with the theoretical predictions. The thermogravimetric analysis (TGA) of oil palm fiber reinforced NR and NBR composites were investigated. The effects of fiber treatment and fiber loading on the thermal behavior of the composites have been evaluated. Thermal conductivity, diffusivity and specific heat of natural rubber and nitrile rubber/oil palm fiber composites were investigated as a function of filler concentration and fiber surface treatments. The use of chemically treated oil palm fibers caused an increase in the thermo physical properties of the composites irrespective of the nature of the chemical treatments.

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5.1 Introduction

In recent years a number of industrial sectors, including automotive, building and aerospace industry have shown immense interest to natural fibers in order to replace glass fibers as reinforcement in composites for structural application (1, 2). Dynamic mechanical analysis (DMA) has been widely employed to investigate the viscoelastic behavior and damping characteristics of various polymeric materials (3, 4). The test measures the response of a material as it is deformed under a sinusoidal or other periodic stresses (5,6). Dynamic mechanical analysis (DMA) has been widely employed for determining the interfacial characteristics of heterogeneous polymeric systems (7, 8). A clear understanding of the time temperature dependant dynamic parameters such as storage modulus, loss modulus and damping factor provides an insight in to the level of interactions between the polymer matrix and fiber reinforcement. It gives us an understanding regarding the viscoelastic behavior of molten polymeric materials and the glass transition region of the composites (9, 10). Storage modulus gives an insight into the stiffness behavior and load bearing capability of composite material (11, 12). Loss modulus is proportional to the amount of energy that has been dissipated as heat by the material. Tan δ is related to the degree of molecular mobility in the polymeric material. The glass transition temperature $T_g$ can be defined as the maximum of the transitions in the loss modulus or tan δ curve at low frequencies (13, 14). Thomas and co-workers done extensive works on the viscoelastic properties of natural fiber composites (15-19).

Jacob et al. (20) studied the dynamic behavior of sisal/oil palm hybrid fiber reinforced natural rubber composites. The storage modulus was found to increase with weight fraction of fiber. In the case of chemically modified fibers, storage modulus and loss modulus were found to vary as a
function of the fiber surface modification. Martins and Mattoso (21) studied the viscoelastic characteristics of sisal fiber reinforced tire rubber composites. They showed that mercerization/acetylation treatment increases dynamic mechanical properties. The results showed that these composites are potential for non-structural applications. The stabilizing effect of lignin filler on NR was examined by Kosikova et al. (22) by using DMA. It is observed that the dynamic mechanical properties of NR vulcanisates were considerably improved by the addition of lignin. Dynamic mechanical studies of short melamine fiber reinforced NBR composites were studied by Rajeev et al. (23). In the case of composites prepared using Resorcinol-hexa-silica bonding system showed significant improvement in storage and loss modulus values.

Thermogravimetric analysis (TGA) is an important analytical method in understanding the structure property relationship and mastering the technology for molecular design and industrial production of different polymeric materials, especially fiber reinforced composites. Moreover, it is a useful technique to determine the thermal stability of the materials. Information can be obtained about the amount of moisture and volatiles present in the composites from TGA. In order to achieve dramatic improvements in the performance of rubber materials, the development of carbon nanotube (CNT)-reinforced rubber composites was performed by Sui et al. (24). Thermal and mechanical properties of the CNT/NR nanocomposites were studied. The thermal properties of microwave curing of natural fiber reinforced composites was investigated by Sgriccia et al. (25). Thermogravimetric analysis of composites obtained from sintering of rice husk–scrap tire mixtures was investigated by Stefani et al (26).

Natural fibers reinforced polymer composites are considered as replacement for metals or carbons in situations where they have better
mechanical properties. But the thermal properties of these composites are in general much lower than that of metals. Consequently, it is more difficult to dissipate the heat and in some situations, this can be an important consideration, particularly if electronic components are situated very close to the material. Thermal conductivity is obviously of importance in the design of products, which will have a thermal insulation function and also in the design of rubber processing equipment. Thermal conductivity, thermal diffusivity and heat capacity are important thermo physical properties of engineering and analysis of rubber and plastic parts. Thermal diffusivity describes the time-dependent non-steady-state aspects of heat flow. Thermal conductivity is a bulk property analogous to mechanical modulus. Moreover, it is well accepted that a mathematical analogy exists between thermal conduction and elasticity of fiber composites. Many theoretical and empirical models have been proposed to predict the effective thermal conductivity of short fiber composites (27-28). For composite materials like reinforced rubber, the thermal diffusivity besides temperature and composition; depends up on the size, structure and pattern of the arrangement of the reinforcement as well as upon the contact thermal resistance between individual components. The thermal conductivity, diffusivity and specific heat of polyester/natural fiber (banana/sisal) composites as function of filler concentration and for several fiber surface treatments was investigated by Idicula et al. (29). Effect of fiber loading and chemical treatments on thermo physical properties of banana fiber/polypropylene commingled composite materials was studied by Sherely et al. (30).

The present chapter deals with the dynamic mechanical properties of oil palm macro/micro fiber reinforced NR and NBR composites with reference to fiber loading and modification. The effect of frequency on viscoelastic properties is also analysed. Cole-Cole plots were drawn to
understand the heterogeneous nature of the composites. The thermal and thermophysical properties of the composites have also been investigated.

5.2 Results and Discussion

5.2.1 Dynamic mechanical properties of oil palm macro fiber reinforced NR composites.

5.2.1.1 Storage modulus

The variation of storage modulus with temperature can be seen in Fig. 5.1. A clear understanding of storage modulus vs. temperature curve provides valuable information about the stiffness of a material, degree of cross linking and fiber/matrix interfacial bonding. It can be seen that storage modulus increases with the increasing oil palm fiber content when compared to the matrix. In all the composites, $E'$ decreased with the increase in temperature and the significant fall is observed in the region between $-60^\circ C$ and $-40^\circ C$. In the glassy region the components are in a frozen state and are highly immobile. So that storage modulus value does not show much variation. When temperature increases the substance becomes more mobile and loses their close packing arrangement and as a result the modulus decreases. But at higher temperature the modulus values vary as a function of fiber content and are maximum for the composites having fiber loading of 30phr (NRF30). In composites, the greater degree of stress transfer at the interface is controlled by the fiber/matrix interaction. The natural rubber comprising only the rubber phase gives the material more flexible character resulting in a low degree of stiffness of material and hence low storage modulus. At low fiber loading the matrix is not restrained by enough fibers and highly localized strains occur in the matrix at low stresses, causing the bond between the matrix and fiber to break leaving the matrix diluted by non-reinforcing debonded fibers. As the fiber concentration increases (30phr), the stress is more evenly distributed and the composite strength and modulus increases.
5.2.1.2 Loss modulus

Loss modulus is a measure of the energy dissipated or lost as heat per cycle of sinusoidal deformation, when different systems are compared at the same strain amplitude. It is in fact the viscous response of a material. The variation of $E''$ with temperature can be seen in Fig. 5.2.

It can be seen that loss modulus shows a slight shift towards higher temperature as fiber loading increases. The maximum heat dissipation occurs at the temperature where $E''$ is maximum, indicating the $T_g$ of the system. The unfilled compound showed $E''$ peak ($T_g$) at $-52.6^\circ$C. As seen in the figure, with increase in fiber loading slight broadening of loss modulus peaks occurred and the $T_g$ value shifted slightly to higher temperature for 30phr fiber reinforced composite (Table 5.1).
Figure 5.2  Loss modulus Vs temperature curves of oil palm macro fiber/Natural rubber composites having various fiber contents

Table 5.1  Peak height, $T_g$ from tan$\delta$ and $E''$ and activation Energy of the composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak height (tan$\delta_{\text{max}}$)</th>
<th>$T_g$ ($^0\text{C}$) obtained from tan$\delta_{\text{max}}$</th>
<th>$E''_{\text{max}}$</th>
<th>Activation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>2.65</td>
<td>-46.4</td>
<td>-52.6</td>
<td>258.24</td>
</tr>
<tr>
<td>NRF30</td>
<td>1.19</td>
<td>-45.8</td>
<td>-51.7</td>
<td>258.12</td>
</tr>
<tr>
<td>NRM30</td>
<td>1.18</td>
<td>-45.4</td>
<td>-51.3</td>
<td>312.84</td>
</tr>
<tr>
<td>NRMS30</td>
<td>1.11</td>
<td>-44.01</td>
<td>-50.2</td>
<td>369.68</td>
</tr>
<tr>
<td>NRMH30</td>
<td>1.15</td>
<td>-44.48</td>
<td>-50.8</td>
<td>350.24</td>
</tr>
</tbody>
</table>

This could be due to the increase in energy absorption caused by the addition of fibers. Also the interphase between the fiber and matrix is in a different physical state from the rest of the matrix, thus counteracting the molecular mobility.
5.2.1.3. Damping factor

Tan\(\delta\) is a damping term that can be related to the impact resistance of a material. As the damping peak occurs in the region of glass transition where the material changes from a rigid to a more elastic state, it is associated with the movement of small groups and chains of molecules within the polymer structure, all of which are initially frozen in. Therefore higher the tan \(\delta\) peak value, greater is the degree of molecular mobility (31).

The variation of tan\(\delta\) of the composites as a function of temperature is given in Fig. 5.3. The gum compound has the highest tan\(\delta\) value, indicating a large degree of molecular mobility. The damping peak of the composites showed a decreased peak height with increased filler loading and is clear from the Table 5.1. This is because the fibers carry a greater extent of stress and allow only a small part of it to strain the interface. Therefore lesser energy dissipation will occur in the composite, where matrix to fiber interaction is strong, whereas greater energy dissipation will occur in the rubber matrix. Incorporation of fibers acted as barriers to the mobility of rubber chains, leading to lower flexibility, lower degrees of molecular motion and hence lower damping characteristics. Lesser the interfacial adhesion between fiber and matrix, greater the damping (32). As seen in Fig. 5.3, at higher fiber loading (30phr), interface between fiber and rubber matrix is stronger, chain flexibility is arrested and \(T_g\) shifts slightly towards higher temperature region. Therefore we can conclude that the presence of natural fibers decreases the damping of the composites (33).
Figure 5.3  Tanδ vs temperature of oil palm macro fiber/natural rubber composites having various fiber contents

5.2.1.4 Estimation of constrained polymer layer

Micro composites generate a great deal of interest from material scientists because of their potentially novel properties. It is important to study the mobility of polymers inside the fillers and also how the presence of fibers affects the mobility of the surrounding polymers. Dynamic mechanical analysis (DMA) was used to study the chain mobility. During the glass transition, the long range polymer chain gains mobility and this dissipates a great amount of energy through viscous movement. This is shown in the tanδ peak. Therefore, any depression in the tanδ indicates the reduction of the number of the mobile chains during the glass transition. The relative peak height is proportional to the volume of the constrained chains (34). The quantitative measurement of constraint chains was developed to study the crystallinity of semi crystalline polymers. The
measurement was used to calculate the constrained polymer volume in a polymer-fiber composite. It is calculated using the equation (35)

$$C = 1 - (1 - C_0) \frac{W}{W_0} \quad [5.1]$$

Where $W_0$ is the energy fraction loss of matrix

$$W = \frac{\Pi \tan \delta}{\Pi \tan \delta + 1} \quad [5.2]$$

It may be noted that the presence of fibers immobilizes a significant amount of polymer chains during the glass transition. A structural model (Fig. 5.4) is proposed to understand the cross linking characteristics of the polymer-fiber composites. In this model, the matrix and the filler bonded each other and form a new phase. These phase reduce the mobility of the surrounding polymers. There is an effective constraint length, and polymers lose their mobility during glass transition when the polymer chain is within this constraint length. The dispersed fibers and the constrained phase form an effective particle with an effective volume much higher than that of the fiber. It is assumed that the fiber surface bonded with the segments of the polymer. These polymer segments are embedded between the fibers. As these polymer segments are parts of polymer chains, the involved polymer chains are also constrained. The effective constrained polymer volume is much higher because of this extended constraint zone.

![Figure 5.4 Schematic of the proposed morphology of fiber composites](image)
The constrained polymer chain volume (C) is plotted against fiber loading (Fig. 5.5). The C values increases with increase of fiber loading. This clearly indicates the presence of polymer chain immobilized as a result of interaction between fiber and matrix.

![Graph showing variation of constraint chain volume against fiber loading](image)

**Figure 5.5** Variation of constraint chain volume against fiber loading

### 5.2.2 Effects of micro fiber on dynamic properties

All plant fiber consists of micro fibrillated cellulose whose diameter is about 2-10 µm with a high aspect ratio. Cellulose micro fibrils reinforced rubber composites has also extremely excellent mechanical properties due to its crystal structure. Dufresne et al. (36) explained that nano composites materials from microcrystalline starch reinforced thermoplastic matrix have good dynamic mechanical properties. Agnes et al. (37) indicated that chemical modification of fibers has profound influence on the dynamic mechanical properties of composites. The cellulose micro fibrils prepared by STEX (alkali treatment), has improved surface characteristic properties, since hemi cellulose, lignin, pectin and other impurities are removed. Thus
the cellulose micro fibrils become rough and have a good surface topography. The extent of these microfilaments in fibril network and the adhesion properties of the matrix with the micro fibrils are the major factors contributing to the overall dynamic properties of the composites.

5.2.2.1 Storage modulus

Figure 5.6 represents the variation of storage modulus against temperature of micro fibril reinforced rubber composites. It can be seen that $E'$ increases moderately with increasing micro fibril content at all temperatures when compared to the gum. During continuous mercerization of fibers by steam explosion, the fibrils become more rough, the moisture absorbing capacity of fibrils are reduced, leading to improved wetting which produces strong interfacial adhesion with the rubber matrix giving rise to a much stiffer composite with higher modulus(38).

![Figure 5.6](image)

**Figure 5.6** Storage modulus vs temperature of oil palm micro fiber/natural rubber composites having various fiber contents
The increased surface area of micro fibrils results in increased cross links with the rubber matrix which contributes to higher $E'$ values. In the case of macro fibers due to the presence of lignin, hemi cellulose etc. fiber/matrix interaction is weak which results in lower $E'$ values.

### 5.2.2.2 Comparison of macro and micro fiber reinforced NR composites

![Graph](image)

**Figure 5.7** Storage modulus vs temperature of oil palm macro and micro fiber/natural rubber composites (30phr)

Figure 5.7 shows storage modulus of oil palm macro and micro fiber reinforced NR composites at 30phr loading. Micro fiber reinforced NR composites shows moderate increase in $E'$ values when compared to macro composites. This confirms that the interfacial adhesion between micro fiber and rubber is better than macro fibers.
5.2.2.3 Loss modulus

The variation of loss modulus with temperature of different micro fibril loading is given in Fig. 5.8. It can be seen that loss modulus peak increased with increase in micro fibril content. The composite containing 30phr micro fibrils (NRM30) show the maximum loss modulus. The $T_g$ values shifted slightly towards higher temperature for 30phr micro fibril composite, which is higher than macro composite (Table 5.1). We also observed that as fibril concentration increases, $T_g$ shifts slightly to higher temperature. The micro fiber reinforced composites show higher loss modulus and stiffness due to greater interfacial interaction.

![Figure 5.8](image_url)

**Figure 5.8** Loss modulus Vs temperature curves of oil palm micro fibril/Natural rubber composites having various fiber contents
5.2.2.4 Comparison of macro and micro fiber reinforced NR composites

![Composite Graph](image)

**Figure 5.9** Loss modulus Vs temperature curves of oil palm macro and micro fibril/ Natural rubber composites (30Phr)

Loss modulus of micro fiber reinforced NR composites is moderately higher than macro composites (Fig. 5.9).

5.2.2.5 Dissipation factor

The variation of tanδ with temperature is given in Fig. 5.10. As seen in the figure, micro fibril (30phr) reinforced rubber composite possesses lower damping capabilities. In the case of 30phr micro composite (NRM30), the tan δ value decreased. Also the Tg value shows a slight shift to higher temperatures for 30phr micro fibril composite, which is higher than macro composite (Table 5.1). The reason why alkali treated micro
fibril composites have lower tanδ is because of strong and rigid micro fibril/rubber interface due to improved adhesion, which reduces molecular mobility in the interfacial zone. Molecular motion along the rubber macromolecular chain is severely hindered which results in low damping properties. Therefore we can conclude that cellulose micro fibrils decrease the damping of the composite. The reason why micro fiber reinforced composites show moderate increase in storage modulus and low tanδ (Fig. 5.11) compared to macro composites is because of the strong and rigid fiber/ matrix interaction in micro composites. Thus micro fiber reinforced composites exhibit better dynamic properties than macro composites.

Figure 5.10 Tanδ vs temperature of oil palm micro fiber/natural rubber composites having various fiber contents
5.2.3 Effects of chemical modification on dynamic properties

5.2.3.1 Storage modulus

The dynamic mechanical properties of composites are very much influenced by the chemical treatment given to the micro fibril surface. The effect of chemical treatments on the storage modulus of micro fibril-reinforced composite is given in Fig. 5.12. It is clear that an improvement in the storage modulus is observed for chemically treated micro composites which are due to the increase in the interfacial stiffness achieved through more intense micro fibril-matrix interaction. i.e., there exits a better interfacial adhesion between the fibrils and the matrix. As seen in the figure, maximum storage modulus is shown by the composite in which fibrils are treated with silane coupling agent (NRMS30) followed
by fibrils treated with benzoyl chloride (NRMB30) followed by resorcinol-silica bonding system (NRMH30). The increase in adhesion in silane treated micro composite is attributed to the decreased hydrophilic nature of treated fibrils, which improves the interaction with the hydrophobic NR matrix. The hydrolyzed silanols form strong covalent bond or hydrogen bond with –OH functional group of cellulose. The individual coupling agent molecules attached to cellulose micro fibrils form a continuous network structure. In addition, the treated surface is very rough and had a number of voids that provides better mechanical interlocking with the NR matrix. The coupling and bonding agents increase the fibril/matrix adhesion causing lesser molecular mobility in the interfacial region. Since the fibrils are well dispersed in the matrix, formation of more cross-links between fibril network and rubber matrix is possible, leading to a stiffer composite. For the alkali treated composite, the moisture absorbing capacity of fibrils is reduced leading to improved wetting, which produces a strong interfacial bond with the rubber matrix giving rise to a stiffer composite with high E' values. In the case of benzoylated fibril composites, the improvement in interfacial adhesion is attributed to the presence of phenyl structure, which enhances bonding between fibril surface and NR matrix. The reduction in hydrophilic nature makes the fibril more compatible with hydrophobic NR and the rough surface improves the mechanical interlocking of the NR molecules with the fibrils and shows better fiber matrix adhesion.
Figure 5.12 Storage modulus vs temperature of treated oil palm micro fiber/natural rubber composites

A hypothetical model of interface of NR-alkali treated and NR-silane treated micro fibril composite is shown in Fig. 5.13 (a) and (b) respectively. For the alkali treated composite, the moisture absorbing capacity of fibrils is reduced leading to improved wetting, which produces a strong interfacial bond with the rubber matrix giving rise to a stiffer composite with high $E'$ values.
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(a)

(b)
A hypothetical model of the interface of (a) alkali treated oil palm microfibril/NR composite (b) interface of silane treated oil palm microfibril / NR composite (c) interface of benzoylated oil palm microfibril / NR composite

A hypothetical model of interface of NR benzoylated microfibril composite is given in Fig. 5.13 (c). In the case of benzoylated treated fibril composites, the improvement in interfacial adhesion is attributed to the presence of phenyl structure, which enhances bonding between fibril surface and NR matrix. The reduction in hydrophilic nature makes the fibril more compatible with hydrophobic NR and the rough surface improves the mechanical interlocking of the NR molecules with the fibrils and improves the adhesion between fibril and matrix. In the case of macro composites, the interfacial adhesion between fiber and matrix is weak due to the presence of lignin, hemicellulose which results in low E’ values. Thus we can conclude that treated microfibril composites had higher values of storage modulus than micro composites.
The effectiveness of fillers on the moduli of the composites can be represented by a coefficient $C$ such as (39)

$$C = \frac{(E'_g / E'_r)_{comp}}{(E'_g / E'_r)_{gum}}$$  \[5.3\]

Where $E'_g$ and $E'_r$ are the storage modulus values in glassy and rubbery region. The higher the values of constant $C$, the lower the effectiveness of the filler. The values of coefficient $C$ are given in Table 5.2. From the table, we can infer that composite NRMS30, in which micro fibrils are silane treated having lower value of coefficient $C$, showing better fiber matrix interaction. Micro composites have lower $C$ constant values than macro composites. We can conclude that chemical treatment increases storage modulus values of micro composites.

<table>
<thead>
<tr>
<th>Composite</th>
<th>Coefficient $C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NRF10</td>
<td>0.90</td>
</tr>
<tr>
<td>NRF20</td>
<td>0.88</td>
</tr>
<tr>
<td>NRF30</td>
<td>0.87</td>
</tr>
<tr>
<td>NRM10</td>
<td>0.86</td>
</tr>
<tr>
<td>NRM20</td>
<td>0.85</td>
</tr>
<tr>
<td>NRM30</td>
<td>0.83</td>
</tr>
<tr>
<td>NRMS30</td>
<td>0.80</td>
</tr>
<tr>
<td>NRMB30</td>
<td>0.82</td>
</tr>
<tr>
<td>NRMH30</td>
<td>0.84</td>
</tr>
</tbody>
</table>
5.2.3.2 Loss modulus

The effect of fibril treatment on variation of loss modulus of composites is depicted in Fig. 5.14. The composite containing fibrils treated with silane coupling agent and resorcinol-silica bonding agent have higher $E''$ values. $T_g$ of treated composites shows a slight shift to higher temperatures. The $T_g$ value of treated microfibril composites is higher than the value of macro composite (Table 5.1). The strong adhesion between treated fibrils and NR matrix results in a much stiffer composite. In the case of macro fibers, because of the presence of hemi cellulose and lignin the adhesion between fiber and matrix is weak. Hence the stiffness of macro fiber composites are lower than micro composites. Thus the loss modulus values of treated micro composites are higher than macro composites.

**Figure 5.14** Loss modulus Vs temperature curves of treated oil palm micro fibril/Natural rubber composites
5.2.3.3 Damping factor

The variation of tanδ of treated micro fibril reinforced composites with temperature is given in Fig. 5.15. Here the chemically treated micro fibril composites have decreased damping characteristics than the macro fiber reinforced composites. The tanδ peak height of silane treated composite (NRMS30) is lower than the value of untreated micro composite NRM30. Among the other treated composites the height of tan δ peak is almost same for all the composites (Table 5.1). The Tg value of treated micro fibril composites shifts slightly to higher temperatures when compared with untreated micro composites. The reason why treated micro composites possess low tanδ is because of strong reinforcement of the matrix by the addition of treated fibrils that are well bonded to the rubber matrix. As a consequence, molecular motion along the rubber macromolecular chain is severely hindered leading to low tanδ values. Hence treated micro fibrils decrease the damping of the composites.

![Figure 5.15 Tanδ vs. temperature of treated oil palm micro fiber/natural rubber composites](image-url)
SEM of tensile fracture surfaces of untreated and treated micro composites are shown in Fig. 5.16 (a) and (b) respectively. In the untreated composites (a) the bonding between rubber matrix and fiber is weak and hence it shows the presence of holes indicating easy fiber pull out, which has taken place due to poor wetting. In the case of the composite containing micro fibrils treated with silane coupling agent (b) the moisture content of the fibrils is greatly reduced. Because of high aspect ratio and surface area of micro fibrils, stronger bonding between fibrils and matrix will take place. This is evident from the short broken fibril ends that can be seen in the micrograph. Thus SEM studies further support the indication of better adhesion by chemical treatment of cellulose micro fibrils.

![Figure 5.16 SEM of tensile fracture surface of (a) untreated micro fiber composite showing fiber matrix debonding and fiber pull out. (b) silane treated micro fiber composite showing good fibril-matrix adhesion](image)

5.2.3.4 Effect of frequency

The storage modulus, loss modulus, and damping peaks are found to be affected by frequency. The variation of $E'$, $E''$, and $\tan\delta$ with temperature at three different frequencies 0.1, 1 and 10Hz of silane treated composite is shown in Fig. 5.17, 5.18 and 5.19 respectively. If a compound is subjected to a constant stress its elastic modulus is expected to decrease
with time due to the molecular rearrangement to minimize the localized stress. Therefore as the frequency increases, there is an increase in $E'$ values. The modulus values found to be decreased as temperature increases from $-70$ to $-40^\circ C$. It can be observed that there was an increase in storage modulus with increase in frequency and this increase is prominent only at low temperatures. This phenomenon may be due to the lesser mobility of the rubber chains when the speed of the cyclic stress is too fast to bring about deformation. The molecules will not get time to undergo permanent deformation (irreversible flow) and so the material exhibits elastic behavior resulting in an increase of $E'$ and $E''$ values.

![Figure 5.17](image.png)

**Figure 5.17** Effect of frequency on $E'$ of silane treated oil palm microfiber/natural rubber composites
Figure 5.18 Effect of frequency on $E''$ of treated oil palm micro fibril (silane)/Natural rubber composites

Figure 5.19 Effect of frequency on $\tan\delta$ of silane treated oil palm micro fiber/ natural rubber composites
As the frequency increased the peak of loss modulus shifted towards higher temperature. The tanδ peak is found to shift to higher temperature with increase of the frequency. The damping peak is associated with the partial loosening of the polymer structure so that groups and small chain segments can move. The tanδ peak, which is indicative of the glass transition temperature, is also indicative of the degree of cross-linking of the system. Increase of frequency is found to have a broadening effect on the tanδ curve.

5.2.3.5 Activation energy for glass transition

The glass transition temperatures of NR composites obtained from tan δ are given in Table 5.1. The table showed that the T_g values of composites are lower than the gum compound. Akay (40) reported that the T_g values obtained from the loss modulus is more realistic than those obtained from damping factor. The activation energy, ΔE for the glass transition of the composite can be calculated from the Arrhenius equation,

\[ f = f_0 \exp\left(\frac{-\Delta E}{RT}\right) \]  \[5.4\]

Where f is the measuring frequency, \( f_0 \) is the frequency when T approaches infinity and T is the temperature corresponding to the maximum of tan δ curve. Table 5.1 gives the activation energy values for the glass transition of NR composites. Among the composites activation energy is highest for silane treated micro fibril composite, indicating better fibril/matrix adhesion and stiffness of the composites.

5.2.3.6 Cole-cole plots

The magnitude of polarization within a material is represented by the dielectric constant, which can be represented by the Debye and Onsagar equations (41). The single relaxation peaks are inadequate to describe the viscoelastic response of polymers. Cole-cole is a particular treatment of dielectric relaxation data obtained by plotting E” against E′, each point
corresponding to one frequency. Structural changes taking place in cross-linked polymers after fiber addition to polymeric matrices can be studied using the Cole-cole method. The dynamic mechanical properties when examined as a function of temperature and frequency are represented on the Cole-cole complex plane, $E = f (E')$. In Cole-cole plot, where the loss modulus data log $E''$ are plotted as a function of the storage modulus log $E'$. The nature of the Cole-cole plot is reported to be indicative of the nature of the system. Homogeneous polymeric systems are reported to show a semi circle diagram (42). The Cole-cole plots of composites NRF30, NRM30 and NRMS30 are depicted in Fig. 5.20. From the figure, it is clear that the composites show a behavior different from homogenous system; this may be due to the presence of macroscopically heterogeneous dispersed fibers and of the different interface effects. The Cole-cole diagrams of different composites shown in the figure are imperfect semi circles. However, the shape of the curve points towards the relatively good fiber/matrix adhesion.

![Cole-cole plot of the macro/micro fiber composites](image)

**Figure 5.20** Cole-cole plot of the macro/micro fiber composites
5.2.3.7 Theoretical prediction of storage modulus

The simplest equation for the reinforcement of a material due to an inclusion is given by Einstein (43). The equation is given by

\[ E_c = E_m(1 + 1.25V_f) \]  \[5.5\]

where \( E \) is the storage modulus, subscripts \( c \) and \( m \) represent composite and matrix; \( V_f \) is the volume fraction of fiber.

Another equation proposed by Einstein is

\[ E_c = E_m(1 + V_f) \]  \[5.6\]

where the terms are the same as explained before.

The Einstein’s theory was modified by Guth (44). The equation proposed is

\[ E_c = E_m(1 + 2.5V_f + 14.1V_f^2) \]  \[5.7\]

The experimental and theoretical storage moduli values at 0.1Hz for varying microfibril loading are given in Table 5.3. It can be seen from the table that at 10% fibril loading, Einstein’s equations show slight negative deviation from the experimental values, Guth equation agree with the experimental values. At 10phr fibril loading Einstein’s model deviate from the experimental values by 6.8 - 7.93% where as at 20% loading they deviate by 6.3 - 8.89%. Thus we can conclude that Einstein’s models approximate the experimental data in the same manner at both micro fibril loading. At 20% loading also Guth model agree with the experimental values.

When the amount of micro fibril is increased to 30phr, Guth model agree the best, Einstein’s equations show deviations from the experimental values. The fiber agglomeration during processing and aspect ratio of micro fibers is not considered in the equations. In the case of various composites, Guth model considered the strong interfacial adhesion
between the matrix and micro fibrils. The stiffness of the composite increases and this factor is also considered in Guth model.

Table 5.3  Experimental and theoretical storage moduli value at 0.1Hz for different loadings

<table>
<thead>
<tr>
<th>Composite</th>
<th>Storage modulus x 10^8(Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental value</td>
</tr>
<tr>
<td>NR</td>
<td>8.825</td>
</tr>
<tr>
<td>NRM10</td>
<td>8.985</td>
</tr>
<tr>
<td>NRM20</td>
<td>9.116</td>
</tr>
</tbody>
</table>

5.2.4 Thermal properties

The thermal analysis of polymers has become a widely used technique for determining the interfacial characteristics of heterogeneous polymeric systems. Thermal behavior of polymers is a useful technique to determine the thermal stability of the materials. It provides information on enthalpy changes associated with heating, annealing and crystallization of polymers (45). It plays a major role in the manufacture of polymeric materials in many consumer-oriented applications. Molding articles and their end uses need a detailed study of the thermal degradation of polymers. In addition, it is possible to quantify the amount of moisture and volatiles present in the composites that have a deteriorating effect.

Incorporation of plant fibers in to different polymeric matrices increases the thermal stability of the systems. In the case of cellulosic fibers, lignin degradation sets in at around 200°C and other polysaccharides mainly cellulose and hemicellulose are oxidized and degraded at higher temperatures (46). Most of the natural fibers lose their strength at about 160°C. Thermal properties of cellulose fibers have been
carried out and the effects of orientation, crystallinity and cross linking on the pyrolytic behaviour of cellulose have been reported.

One of the most important methods for studying the thermal properties of polymeric materials is thermo gravimetry (TG). Thermo gravimetric data will give a number of stages of thermal breakdown, weight loss of the material in each stage, threshold temperature etc. Both thermo gravimetry and derivative thermo gravimetry (DTG) will provide information about the nature and extent of degradation of the material. In differential scanning calorimetry the heat flow rate associated with a thermal extent can be measured as a function of time and temperature allowing us to obtain quantitative information about melting and phase transitions of the composite system.

Thermal analysis is an important analytical method used for studying the structural property relationship and mastering of the technology for molecular design and industrial production of different polymeric materials, especially fiber reinforced composites. It is a useful technique to determine the thermal stability of the composites (47). It is also possible to determine the moisture content and the volatiles present, which have deteriorating effect on the composite properties. In the case of cellulose fibers, lignin degrades at around 200°C while other polysaccharidessuch as cellulose are oxidized and degraded at higher temperatures. Most of the natural fibers lose their strength at about 160°C on heating.

Thermogravimetric curves of natural rubber and composites as a function of fiber loading were shown in Fig. 5.21. Thermal decomposition of each sample takes place in a programmed temperature range of 30-600°C. For oil palm fiber, dehydration as well as degradation of lignin occurs in the temperature range 60 to 200°C and most of the cellulose is decomposed at a temperature of 350°C. For NR, the peak at 360°C corresponds to the
degradation of rubber matrix. From the figure, it is clear that fiber filled system degrades later than NR matrix, i.e., the thermal stability of the composite is higher than that of the matrix. This increased stability of composite is due to improved fiber matrix interaction. Derivative thermogravimetric curves (DTG) also give evidence for this (Fig. 5.22). The major DTG curve of NR is observed at 360°C, which indicates the degradation of saturated and unsaturated carbon atoms in NR. From Fig. 5.21, it is clear that the peak in the case of oil palm fiber-NR composite is shifted slightly to higher temperature region compared to NR matrix, suggesting that the thermal stability of the composite is more compared to pure NR due to better fiber-matrix interaction. The major source of stability in cellulose is due to hydrogen bonding which allows thermal energy to be distributed over many bonds. From Fig. 5.23 it is evident that micro fiber reinforced NR composites are thermally more stable than macro composites.

Weight loses of NR, cellulose and composites at different temperatures are given in Table 5.4. Step analysis of NR and composites shows a percentage mass drop of 0 to 7% from 30-100°C. At 200°C, 1.2% mass drop for composites due to the degradation of lignin from fiber and 10% mass drop of cellulose. At 400°C the weight loses for NR and oil palm-NR composite are 54.8, 48.4 and 42.3 (silane) respectively. Pure cellulose has a mass drop of 63.5%. At a temperature of around 500°C, NR is completely decomposed. At 500°C, the weight losses for the untreated composite and silane treated composite are 92.4 and 90.1 respectively. It is found in the case of chemically modified oil palm – NR composites, the extent of degradation at a given temperature is found to be less than untreated composites. The TGA and DTG curves of treated micro composites are given in Fig. 5.24 and 5.25. From this figures, it is clear that the degradation temperature is shifted to slightly higher temperature in the case of treated composites. This is due to the improved
fiber/matrix adhesion as a result of the formation of bonds existing between fiber and matrix provided by the coupling agent.

**Figure 5.21** Thermograms of oil palm microfiber reinforced NR composites as a function of fiber loading

**Figure 5.22** Derivative thermograms of oil palm microfiber reinforced NR composites as a function of fiber loading
Figure 5.23 Thermograms of macro and micro fiber composites

Figure 5.24 Thermograms of treated oil palm microfiber reinforced NR composites
Figure 5.25 Derivative thermograms of treated oil palm microfiber reinforced NR composites

Table 5.4 Weight losses at different temperatures

<table>
<thead>
<tr>
<th>Temperature°C</th>
<th>Weight losses (%)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NR cellulose</td>
<td>NRM30</td>
<td>NRMS30</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>7.9</td>
<td>1.2</td>
<td>1</td>
</tr>
<tr>
<td>200</td>
<td>0</td>
<td>10.4</td>
<td>2.2</td>
<td>2.4</td>
</tr>
<tr>
<td>400</td>
<td>54.8</td>
<td>65.7</td>
<td>48.4</td>
<td>42.3</td>
</tr>
<tr>
<td>500</td>
<td>100</td>
<td>81</td>
<td>92.4</td>
<td>90.1</td>
</tr>
</tbody>
</table>

5.2.5 Thermo physical properties of NR composites

In order to explain the behavior of the effective thermal conductivity of the composite, we need thermal conductivity values of its constituents, i.e., fiber and matrix. Addition of fillers and reinforcements changes the thermal properties of the polymers. The dispersion of the filler particles, orientation, fiber aspect ratio, relative modulus of the fiber and matrix and thermal expansion mismatch affect the thermal properties of the composite (48). The thermal conductivity and diffusivity measurements are presented in Table 5.5 with their associated uncertainties for the natural rubber and the composite.
samples loaded with oil palm fibers. The specific heat and the density measurements are also given in the same table. It can be seen from the table that when macro fibers are added to NR matrix, we noted a significant increase of both thermal conductivity and thermal diffusivity (i.e., from 0.128 \( \text{Wm}^{-1}\text{K}^{-1} \) for neat NR matrix to 0.141 \( \text{Wm}^{-1}\text{K}^{-1} \) for macro composite. The macro fibers are washed with 2\% NaOH. Sodium hydroxide concentration has an influence on the thermophysical properties of the composites (49). Thermal conductivity and diffusivity of NaOH treated micro fiber composites are higher than NR matrix. NaOH treatment removes certain amount of lignin, wax and oils covering the external surface of the fiber cell wall.

The following reaction takes place as a result of alkali treatment:

\[
\text{Fiber—OH} + \text{NaOH} \rightarrow \text{Fiber—ONa}^+ + \text{H}_2\text{O} \quad [5.8]
\]

The effect of chemical treatment of the oil palm fibers on the thermophysical properties and density values of the composites are given in Table 5.5 with their uncertainties. It can be seen that both thermal conductivity and diffusivity values of the steam exploded (5\% NaOH) micro fiber composites (at 0.50 Vf) are higher than that of the macro fiber composites. This indicates that up on increasing the concentration of NaOH there is an increase in the thermophysical properties of the composites. The effect of alkali on oil palm fiber is a swelling reaction, during which the natural crystalline structure of the cellulose relaxes. When hemicellulose is removed the inter-fibrillar region is likely to be less dense and less rigid and thereby makes the fibrils more capable of rearranging themselves (50). The increase in the percentage of crystallinity index of the alkali treated fibers occurs because of the removal of cementing material, which leads to a better packing of cellulose chains. Treatment of cellulose fibers with alkali brings about the process of swelling and dissolution. The fiber surface shows more fibrillation, which can be attributed to the removal of hemicellulose and lignin. This effect becomes more pronounced as
the concentration of NaOH increases. In the case of micro composites, thermal conductivity and diffusivity increased by 9 to 10% respectively.

When HRH bonding agent is used during composite preparation, there is an increase in thermal conductivity and diffusivity compared to macro fiber reinforced composites. Composite containing HRH bonding agent showed good mechanical properties compared with those of other modifications. Setua et al. (51) studied effect of HRH bonding agent on silk fiber reinforced nitrile rubber composites. They obtained improvement in mechanical properties of the composite. A three-component system consisting of resorcinol, hexamethylene tetra mine and silica was used as a bonding agent for the present system. The three-component system creates an in-situ resin by the condensation reaction between resorcinol and methylene donor, hexamethylene tetramine. In the case of HRH addition, silica forms hydrogen bonding with the hydroxyl group of the fiber and the polyisoprene segments present in the HRH bonding agent improves the compatibility between the fiber and the NR matrix. As a result of this, the interfacial interaction between the fiber and matrix increases. The hydrophilic fiber –OH groups are replaced by the hydrophobic moieties by the hydrogen bonding between the bonding agent and –OH groups of the fiber. This increases the strength of the chemical interlocking of the hydrophobic centers of the rubber and the fibers.

Table 5.5 Thermal conductivity (k), thermal diffusivity (a), specific heat (Cp) and density (ρ) of NR/oil palm composites

<table>
<thead>
<tr>
<th>Material</th>
<th>k (Wm⁻¹K⁻¹)</th>
<th>a (m²s⁻¹) x 10⁻⁷</th>
<th>Cp (J kg⁻¹K⁻¹)</th>
<th>ρ (kg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR Gum</td>
<td>0.128±0.002</td>
<td>0.546±0.02</td>
<td>2414±48</td>
<td>971±10</td>
</tr>
<tr>
<td>NR+30phr macro fiber</td>
<td>0.141±0.002</td>
<td>0.706±0.03</td>
<td>1971±73</td>
<td>1013±28</td>
</tr>
<tr>
<td>NR+30phr micro fiber</td>
<td>0.146±0.002</td>
<td>0.751±0.04</td>
<td>1851±101</td>
<td>1050±31</td>
</tr>
<tr>
<td>NR+30phr micro fiber+Resorcinol-hexa-hydrated silica</td>
<td>0.151±0.003</td>
<td>0.691±0.03</td>
<td>2023±85</td>
<td>1081±19</td>
</tr>
</tbody>
</table>
Many theoretical and empirical thermal models have been proposed to predict the effective thermal conductivity of polymer composite materials (29). In fact, when the ratio between the thermal conductivity values of the matrix and the fibers is lower than 10, a first-order model can be used to estimate the effective thermal conductivity of the composite. In polymer composites, if the alignment of the fibers is parallel to the direction of the thermal flux, the thermal conductivity will be highest (parallel conduction) and if the alignment of the fibers is perpendicular to the direction of the thermal flux, thermal conductivity will be the lowest (series conduction). The simplest alternative is to represent the composite material using two components arranged in either parallel or series with respect to the heat flow. This gives the upper (ksup) and lower (klow) bounds of effective thermal conductivity. The effective thermal conductivity of polymers filled with natural fibers can be represented using simple theoretical models.

Parallel model (2)

\[
ksup = kp (1- \varphi) + k_f \varphi \tag{5.9}
\]

Series model (3)

\[
\frac{1}{k_{inf}} = \frac{1- \varphi}{kp} + \frac{\varphi}{k_f} \tag{5.10}
\]

where \(k_p\) and \(k_f\) are the thermal conductivities of the polymeric matrix and the fibers, respectively, and \(\varphi\) is the fiber volume fraction.

Sherely et al. (30) showed a good agreement between experimental thermal conductivity of banana fiber commingled PP composites and theoretical values computed using the series conduction model. In this case thermal conductivity is measured in the direction transverse to the composite sample plane. Figure 5.26, the experimental data of NR filled with oil palm fibers are plotted as a function of treatment. The use of the
series conduction model [Eq. 5.10] allowed us estimating the transverse thermal conductivity of oil palm fibers. The value obtained is: $k_f = 0.1296 \text{ Wm}^{-1}\text{K}^{-1}$. The curve corresponding to this model was added in Fig. 5.26. We note that the experimental values are in agreement with $k_{inf}$ (Series model). In the case of macro fiber composites, due to fiber agglomeration there is slight deviation from the series model. This result is foreseeable because the thermal conductivity was measured in the transverse direction to the plane of the composite plate. So, in this case, the composite can be seen as a stacking of several fiber layers separated by polymeric matrix. Probably this is a reason of good agreement of the experimental results to the series model; such transversal packing is close to the series type packing in the direction of heat flow.

![Experimental data vs Series model](image)

**Figure 5.26** Comparison of NR/oil palm fibers composites thermal conductivity with series conduction model
5.2.6 Dynamic mechanical properties of oil palm micro fiber reinforced NBR composites.

5.2.6.1 Effects of micro fiber loading on dynamic properties

5.2.6.2 Storage modulus

![Storage modulus Vs temperature curves of untreated oil palm micro fibril/NBR composites having various fiber contents](image)

The variation of storage modulus with temperature at different loading is given in Fig. 5.27. It can be seen that the storage modulus increases with increasing micro fibril content at all temperatures compared with gum. In all the samples, $E'$ decreased with the increase in temperature and the significant fall is observed in the region between $-50^\circ\text{C}$ and $+10^\circ\text{C}$. In the glassy state, the molecular chains are in a frozen state, i.e. highly immobile. These frozen chains results in good stiffness to the composite material and hence high values of storage modulus. When temperature increases the components become mobile and lose their close packing arrangement, hence in the rubbery region $E'$ values decreases. But at higher temperature the modulus value varies as a
function of fiber content and is maximum for the composites having micro fiber loading of 30phr (NBRM30). In composites the degree of stress transfer at the interface is controlled by the fiber/matrix interaction. The nitrile rubber comprising only the rubber phase gives the material more flexible character resulting in a low degree of stiffness of material and hence lower storage modulus value. At low fiber loading the matrix is not restrained by enough fibers and highly localized strains occur in the matrix at low stress, causing the bond between the matrix and fiber to break leaving the matrix diluted by non-reinforcing debonded fibers. As the fiber concentration increases (30phr), the stress is more evenly distributed and the composite strength and modulus increase.

When natural fibers are converted into micro fibrils by steam explosion method (5%NaOH), hemicellulose, pectin and other impurities are removed from the fiber surface. For the alkali treated composites, the moisture absorbing capacity of fibrils is reduced leading to improved wetting which produces a strong interfacial bond with the rubber matrix. Since treated fibrils have more surface area, there is the formation of more cross-links within the rubber matrix fibril network leading to high E' values. Cellulose micro fibrils, because of the presence of many –OH functional group on its surface, is polar in nature. Nitrile rubber too is a polar rubber due to the presence of acrylonitrile group. The above characteristics of the fibrils and the rubber produce excellent adhesion/bonding between the cellulose micro fibers and the nitrile rubber in the composites. Thus when micro fibers are incorporated in to the rubber matrix, stiffness of composite increases, resulting in higher storage modulus. As micro fibril loading increases, E’ value of composite increases. Thus E’ of composite containing 30phr micro fiber is higher than other composites (Fig. 5.27). This is probably due to the increase in the stiffness of the matrix, with the reinforcing effect imparted by the fibrils that allowed a greater degree
of stress transfer at the interface. A hypothetical model of NBR-alkali treated micro fibril composite is given in Fig. 5.28

![Diagram of NBR-alkali treated micro fibril composite](image)

**Figure 5.28** Schematic sketch showing bonding between microfibril and NBR matrix

### 5.2.6.3 Loss modulus

The variation of $E''$ with temperature can be seen in Fig. 5.29. It can be seen that loss modulus values increases with fibril loading. Table 5.6 gives the $E''_{\text{max}}$ values of gum and filled composites. The maximum heat dissipation occurs at the temperature where $E''$ is maximum, indicating the $T_g$ of the system. The gum compound showed $E''$ peak at $\approx 20.98^\circ C$, which was attributed to the mobility of the macromolecular chains. As seen in Fig. 5.29, with increase in fibril loading slight broadening of loss modulus peaks occurred and the $T_g$ value shifted slightly to higher temperatures. This could be due to the increase in energy absorption caused by the addition of micro fibers. Also the inter phase between the fiber and matrix is in a different physical state from the rest of the matrix, thus counteracting the molecular
mobility. The higher modulus is also due to the presence of micro fibrils that reduced the flexibility of the material by introducing constrains on the segmental mobility of polymeric molecules.

![Figure 5.29](image)

**Figure 5.29** Loss modulus Vs temperature curves of untreated oil palm micro fibril/NBR composites having various fibers contents

**Table 5.6** Peak height, T\(\text{g}\) from tan\(\delta\) and \(E''\) and activation energy of the composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Damping factor tan(\delta_{\text{max}})</th>
<th>T(\text{g}) ((^\circ)C) obtained from</th>
<th>Activation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>tan(\delta_{\text{max}})</td>
<td>(E'')</td>
<td></td>
</tr>
<tr>
<td>NBR</td>
<td>1.680</td>
<td>-13.51</td>
<td>-21.36</td>
</tr>
<tr>
<td>NBRM30</td>
<td>0.819</td>
<td>-12.03</td>
<td>-20.22</td>
</tr>
<tr>
<td>NBRSM30</td>
<td>0.823</td>
<td>-12.53</td>
<td>-20.53</td>
</tr>
<tr>
<td>NBRH30</td>
<td>0.801</td>
<td>-11.71</td>
<td>-20.01</td>
</tr>
<tr>
<td>NBRD30</td>
<td>0.816</td>
<td>-11.97</td>
<td>-20.16</td>
</tr>
</tbody>
</table>
5.2.6.4 Damping behavior

Damping term (\(\tan\delta\)) is an effective method to evaluate the interfacial bonding in composites. It was reported that higher damping at the interfaces, the poorer the interfacial adhesion. The damping properties of a material give the balance between the elastic phase and viscous phase in a polymeric structure. The major factors which affects the damping nature are (a) nature of matrix (b) nature of interface (c) damping due to energy dissipation in the area of matrix cracks and broken fibers (d) frictional damping due to slip in the unbound regions between fiber and matrix interface or delaminations. Since the damping peak occurs in the region of glass transition when the material changes from a rigid to a more elastic state, it is associated with the movement of small groups and chains of molecules within the polymer structure, all of which are initially frozen in. Therefore higher the \(\tan\delta\) peak value, greater is the degree of molecular mobility. As seen in Table 5.6 gum compound has the highest \(\tan\delta\) value, indicating a large degree of molecular mobility and so better damping properties.

The variation of \(\tan\delta\) of the composite with temperature is given in Fig. 5.30. It can be seen that \(\tan\delta_{\text{max}}\) decreases with increase in fibril loading. By the addition of cellulose micro fibrils the peak height decreases (Table 5.6). Composite containing 30% micro fiber loading is having only a peak height of 0.84, showing less damping properties.
Figure 5.30  Tanδ Vs temperature curves of untreated oil palm micro fibril/NBR composites having various fibers contents

The incorporation of cellulose micro fibrils is expected to influence the $T_g$ of the matrix by restricting the chain movement of polymer chains, leading to lower flexibility, lower degree of molecular motion, and hence lower damping characteristics. From the figure, we can infer that as fiber loading increases the $T_g$ values are shifted very slightly towards higher temperature region. This envisages that a composite material with very good interfacial bonding between the fibrils and matrix will tend to dissipate lesser energy, showing low magnitude of damping peak in comparison to a material with poorly bonded interface, which is further substantiated by our experimental results. Thus one can conclude that cellulose micro fibrils decrease the damping of the composite.

5.2.6.5 Estimation of constrained polymer layer

Micro composites generate a great deal of interest from material scientists because of their potentially novel properties. It is important to
study the mobility of polymers inside the fillers and also how the presence of fibers affects the mobility of the surrounding polymers. Dynamic mechanical analysis (DMA) was used to study the chain mobility.

Figure 5.31 shows the variation of constrained polymer chain volume (C) against fiber loading. The C values increase with increase of fiber loading. This clearly indicates the increasing concentration of polymer chains constrained as a result of interaction between fiber and matrix with increasing concentration of filler. The C values are higher in the case of NBR composites than NR composites. This shows better fiber/matrix interaction in NBR composites than NR composites.

![Figure 5.31](image-url)  
**Figure 5.31** Variation of constrained polymer chain volume (C) against microfiber loading.
5.2.6.6 Effects of treatment on dynamic properties

5.2.6.7 Storage modulus

The effects of chemical treatments on the storage modulus of microfibril composite are given in Fig. 5.32. From the figure, it is clear that slight improvement in storage modulus is observed for chemically treated micro composites which are due to the increase in interfacial stiffness achieved through more intense micro fibril/matrix interaction. i.e., there exists a better interfacial adhesion between the fibril and matrix. It is evident that E’ values increases with chemical treatment and maximum E’ is exhibited by the composite prepared with micro fibrils treated with resorcinol-silica bonding system.

![Figure 5.32](image_url)

**Figure 5.32** Storage modulus Vs temperature curves of treated oil palm microfibril/NBR composites having various fiber contents.

When highly polar filler such as silica is added to a polar matrix NBR, strong interfacial adhesion between the polar micro fibrils and matrix is possible. The stiffness of the composite increases, hence high values for storage modulus. The formation of more cross links within the rubber
matrix-fibril network also leads to high storage modulus values. The role of resorcinol-hexa-silica bonding system in adhesion between silk fiber and NBR has been studied by Setua et al. (51). In the case of composites prepared with DCP, radical formation is there. This radical induces micro fibril matrix interaction, results in a strong and stiff composite. When micro fibrils are treated with silane and benzoyl chloride, the hydrophilic nature of micro fibrils get reduced and hence lesser adhesion between fibril and matrix. Hence $E'$ values of these composites are lower than other treatments. The effectiveness of fillers on the moduli of the composites can be represented by a coefficient $C$ such as

$$
C = \frac{(E'_g/E'_r)_{\text{comp}}}{(E'_g/E'_r)_{\text{gum}}} \quad [5.11]
$$

Where $E'_g$ and $E'_r$ are the storage modulus values in glassy and rubbery region. The higher the values of $C$, the lower the effectiveness of the filler. The values of coefficient $C$ are given in Table 5.7.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Constant C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBRM10</td>
<td>0.99</td>
</tr>
<tr>
<td>NBRM20</td>
<td>0.98</td>
</tr>
<tr>
<td>NBRM30</td>
<td>0.94</td>
</tr>
<tr>
<td>NBRS30</td>
<td>0.95</td>
</tr>
<tr>
<td>NBRH30</td>
<td>0.89</td>
</tr>
<tr>
<td>NBRD30</td>
<td>0.91</td>
</tr>
</tbody>
</table>

From the table, we can infer that composite NBRH30, in which micro fibrils are treated with resorcinol-silica bonding agent having lower value of coefficient $C$, showing better fiber/matrix interaction. We can conclude that chemical treatment increases storage modulus values of micro composites.
5.2.6.8 Determination of cross link density.

For supporting the better performance of the composite cross link density was determined. The cross-link density can be calculated from the theory of rubber elasticity. The shear modulus \( G \) of a cross linked rubber is given by

\[
G = \frac{\frac{r_1^{-2}}{r_f^{-2}} dRT (1 - 2M_c)}{M_n} \tag{5.12}
\]

where \( d \) is the density, \( R \) is the universal gas constant, \( T \) is the absolute temperature, \( M_c \) is the molecular weight between cross links, \( M_n \) is the chain backbone molecular weight and \( \frac{r_1^{-2}}{r_f^{-2}} \) is the ratio of the mean square end to end distance of the polymer chain in the sample to the same quantity in a randomly coiled chain. At this moment this ratio was assumed to be unity. In the case of highly cross linked systems, the quantity \( 1 - \frac{2M_c}{M_n} \) is a correction factor for chain ends and become negligible when \( M_n \) is very large compared to \( M_c \). Hence equation 5.10 becomes

\[
G = \frac{dRT}{M_c} \tag{5.13}
\]

\( G \) must be measured at the rubbery plateau region above \( T_g \). Shear modulus \( G \) can be taken as \( E'/3 \) and \( E' \) is calculated at \( T_g + 40^\circ C \). Therefore molecular weight between cross links can be measured as

\[
M_c = 3dRT/E' \tag{5.14}
\]

The cross link density can be calculated from the equation

\[
\text{Cross link density} = \frac{1}{2} M_c \tag{5.15}
\]

The variation of cross link density with micro fibril loading is depicted in Fig.5.33. From this we can infer that as fibril loading increases cross link density also increases which supports the increment in the \( E' \) values.
Figure 5.33 Variation of cross link density with fiber content

Figure 5.34 shows the variation of cross link density with chemical modification. It is evident that composites containing fibers treated with HRH bonding agent has the maximum cross link density values as also apparent from the storage modulus values.

Figure 5.34 Variation of cross link density with chemical treatment
5.2.6.9 Loss modulus and damping factor

The variation of loss modulus with temperature of the treated composite is depicted in Fig. 5.35. It can be seen that the loss modulus peak increased with chemical treatment.

![Graph of log E'' vs temperature](image)

**Figure 5.35** Loss modulus Vs temperature curves of treated oil palm micro fibril/NBR composites having various fiber contents.

Table 5.6 shows the $E''_{\text{max}}$ values and $T_g$ of the treated composites. The composite in which resorcinol-silica bonding agent is added exhibits the maximum loss modulus and greater $T_g$. The variation of $\tan\delta$ with temperature is given in Fig. 5.36.
It is obvious that chemically treated composites have lower $\tan\delta$ than untreated composites. The reason why treated composites possess lower $\tan\delta$ is attributed by the better interfacial interactions in treated micro composites, which decreases the polymer chain mobility in the interfacial zone. Another reason is the presence of bonding agents, peroxides, results in more number of cross links being formed and mercerisation leads to strengthening of these cross links. As reported by other authors, a shell of immobilised polymer surrounds the micro fibrils (52). The different physical state of the matrix surrounding the fibrils also hinders the molecular motion. As a result, molecular motion along the rubber macromolecular chain is severely hindered leading to low damping characteristics.

**Figure 5.36** $\tan\delta$ Vs temperature curves of treated oil palm micro fibril/NBR composites having various fiber contents

![Graph showing $\tan\delta$ vs temperature curves for treated oil palm micro fibril/NBR composites with various fiber contents.](image-url)
5.2.6.10 Effect of frequency

The storage modulus, loss modulus, and damping peaks are affected by frequency. The variation of $E'$, $E''$ and $\tan\delta$ with temperature at three different frequencies $0.1$, $1$ and $10$Hz of bonding agent treated composite is shown in Fig. 5.37, 5.38, 5.39 respectively.

**Figure 5.37** Effect of frequency on $E'$ of treated oil palm micro fibril/NBR composites

**Figure 5.38** Effect of frequency on $E''$ of treated oil palm micro fibril/Natural rubber composites
Figure 5.39  Effect of frequency on tanδ of treated oil palm micro fibril/NBR composites

The modulus values are found to be decreased from –60°C to –30°C. It can be observed that there was an increase in storage modulus with increase in frequency and this increase is prominent only at low temperatures. This phenomenon may be due to the lesser mobility of the rubber chains when the speed of the cyclic stress is too fast to bring about deformation. The molecules will not get time to undergo permanent deformation (irreversible flow) and so the materials exhibits elastic behavior resulting in an increase of E’ and E” values. The tanδ peak was shifted to a higher temperature with increase in frequency. The damping peak, which is indicative of the glass transition temperature, is also indicative of the extent of cross-linking of the system. Increase of frequency is found to have a broadening effect on the tanδ curve. Broadening of the curve is due to some kind of heterogeneity in the network structure. The introductions of fibers affect the curing reaction, affects the molecular motions and diffusion as well.
5.2.6.11 Energy of activation for glass transition

The activation energy, $\Delta E$ for the glass transition of the composite can be calculated from the Arrhenius equation,

$$f = f_0 \exp \left( \frac{-\Delta E}{RT} \right)$$  \[5.16\]

where $f$ is the measuring frequency, $f_0$ is the frequency when $T$ approaches infinity and $T$ is the temperature corresponding to the maximum of tan$\delta$ curve. Table 5.6 gives the activation energy values for the glass transition of NBR composites. Among the composites activation energy is highest for HRH treated micro fibril composite, indicating better fibril/matrix adhesion and stiffness of the composite.

5.2.6.12 Cole-cole plot

The magnitude of polarization within a material is represented by the dielectric constant, which can be represented by the Debye and Onsagar equations. The single relaxation peaks are inadequate to describe the viscoelastic response of polymers. Cole-cole is a particular treatment of dielectric relaxation data obtained by plotting $E''$ against $E'$, each point corresponding to one frequency. Structural changes taking place in cross-linked polymers after fiber addition to polymeric matrices can be studied using the Cole-cole method. The dynamic mechanical properties when examined as a function of temperature and frequency are represented on the Cole-cole complex plane. $E = f(E')$. In Cole-cole plot, where the loss modulus data (log $E''$) are plotted as a function of the storage modulus (log $E'$). The nature of the Cole-cole plot is reported to be indicative of the nature of the system. Homogeneous polymeric systems are reported to show a semi circle diagram. The Cole-cole plots of composites NBRM30, NBRMH30 and NBRMD30 are depicted in Fig. 5.40.
From the figure, it is clear that the composites show behavior different from homogenous system, may be due to the presence of macroscopically heterogeneous dispersed fibers and of the different interface effects. The Cole-cole diagrams of different composites shown in the figure are imperfect semi circles. However, the shape of the curve points towards the relatively good fiber matrix adhesion.

**5.2.6.13 Morphology**

The extent of fiber matrix adhesion and morphology of tensile fracture surfaces was analyzed. SEM of tensile fracture surfaces of micro fiber treated composites are shown in Fig. 5.41 (a, b, c, d, e).
Figure 5.41 (a-e): SEM of various treated microfibrill reinforced NBR composites (a) NaOH treated composite (b) Silane treated composite (c) Benzoylated composite (d) Composite modified by HRH bonding agent (e) Peroxide treated composite
In the micro composites (b, c) fibrils treated with benzoyl chloride and silane coupling agent, the bonding between rubber matrix and fiber is weak and hence it shows the presence of holes indicating easy fiber pull out, which has taken place due to poor wetting. In the case of the composite containing micro fibrils treated with NaOH (a), HRH bonding agent (d) and peroxide (e) the moisture content of the fibrils is greatly reduced. Because of high aspect ratio and surface area of micro fibrils, stronger bonding between fibrils and matrix will take place. This is evident from the short broken fibril ends that can be seen in the micrograph. Thus scanning electron microscopic studies further supports the indication of better adhesion by chemical treatment of cellulose micro fibrils.

5.2.6.14 Theoretical prediction of storage modulus

The simplest equation for the reinforcement of a material due to an inclusion is given by Einstein. The equation is given by

\[ E_c = E_m (1 + 1.25V_f) \]  \[5.17\]

Where \( E \) is the storage modulus, subscripts c and m represent composite and matrix, \( V_f \) is the volume fraction of fiber. Another equation proposed by Einstein is

\[ E_c = E_m (1 + V_f) \]  \[5.18\]

Where the terms are the same as explained before. The Einstein’s theory was modified by Guth. The equation proposed is

\[ E_c = E_m (1 + 2.5V_f + 14.1V_f^2) \]  \[5.19\]

The experimental and theoretical storage moduli values at 0.1Hz for varying microfibril loading are given in Table 5.8.
Table 5.8  Experimental and theoretical storage moduli value at 0.1Hz for different loadings

<table>
<thead>
<tr>
<th>Fibril loading (%)</th>
<th>Storage modulus x 10^8 (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental value</td>
</tr>
<tr>
<td>NBR</td>
<td>8.825</td>
</tr>
<tr>
<td>NBRM10</td>
<td>8.985</td>
</tr>
<tr>
<td>NBRM20</td>
<td>9.116</td>
</tr>
</tbody>
</table>

It can be seen from the table that at 10% fibril loading, Einstein’s equations show slight negative deviation from the experimental values, Guth equation agree with the experimental values. At 10phr fibril loading Einstein’s model deviate from the experimental values by 6.8-7.93 % where as at 20%loading they deviate by 6.3-8.89%. Thus we can conclude that Einstein’s models approximate the experimental data in the same manner at both micro fibrils loading. At 20% loading also Guth model agree with the experimental values. When the amount of micro fibril is increased to 30phr, Guth model agree the best, Einstein’s equation’s show deviations from the experimental values. Thus it is clear that Guth model considered the strong interfacial adhesion between the matrix and micro fibrils. The stiffness of the composite increases and this factor is also considered in Guth model.

5.2.7 Thermal properties

The thermograms of the oil palm fiber reinforced nitrile rubber composites as a function of fiber loading are shown in Fig. 5.42. The
temperature range used for the analysis is 100-600°C. For the gum composite the peak at about 350°C corresponds to the maximum degradation of the rubber matrix. In the case of micro fiber filled system, the major degradation starts at 300°C and is almost over at a temperature of 515°C, showing that the thermal stability of the composite is higher than that of the matrix. This increased stability is due to improved micro fibril/matrix interaction. Derivative thermogravimetric curves (DTG) also give evidence for this (Fig. 5.43).

*Figure 5.42* Thermograms of oil palm/NBR composites as function of fiber loading
Figure 5.43 Derivative thermograms of oil palm microfiber reinforced NBR composites as a function of fiber loading

Figure 5.44 Thermograms of treated oil palm microfiber/NBR composites
Composites containing chemically treated micro fibers were thermally more stable than untreated composite and among the composites containing chemically treated composites, composites treated with resorcinol bonding agents were found to be more stable (Fig.5.44). This was also substantiated in the increase of decomposition temperatures of hemicelluloses and α-cellulose for the treated composites (53).

The major peak in the DTG curve of NBR is observed at 400°C, which indicates the degradation of saturated and unsaturated carbon atom in NBR. In micro composites two peaks are obtained, a minor peak at 300°C corresponds to degradation of cellulose and a major peak at 450°C points to the degradation of dehydro cellulose. It is evident from the Fig. 5.43 that thermal stability of composite is higher than those of the matrix as the major peak of microfibril/NBR composite is inclined to slightly to higher temperature side.

Step analysis of thermogravimetric scan of neat NBR, NBRM30 and NBRMH30 composites showed that there is no mass drop at 100°C. But at 400°C, the major drop for composites are 95, 10, 8% respectively. At a temperature around 400°C NBR is completely decomposed. Weight loss of NBR and micro composite at different temperatures are given in Table 5.9.

The TGA curves of treated micro composites are given in Fig. 5.44. From the figure, it is clear that the degradation temperature is shifted to slightly higher region in the case of treated composites than that of untreated ones. This is due to the improved fiber/ matrix adhesion as a result of the formation of bonds existing between fiber and matrix provided by the bonding agents. At 500°C the weight loss of the untreated composite containing 30% fiber and bonding agent (HRH) are 91 and 88 respectively. The increase in thermal stability in the case of HRH bonding is due to the additional intermolecular bonding between fiber and matrix.
associated with the formation of covalent bond between resorcinol and OH group of cellulose.

Table 5.9 Weight losses at different temperatures

<table>
<thead>
<tr>
<th>Temperature°C</th>
<th>Weight losses (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NBR</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>200</td>
<td>0</td>
</tr>
<tr>
<td>400</td>
<td>95</td>
</tr>
<tr>
<td>500</td>
<td>100</td>
</tr>
</tbody>
</table>

5.2.8 Thermo physical properties of NBR composites

The thermal conductivity and diffusivity measurements of oil palm fiber reinforced NBR composites are presented in Table 5.10 with their associated uncertainties for the nitrile rubber and the various composite samples. The specific heat and the density measurements are also given in the same table. When nitrile rubber is reinforced with oil palm macro fiber (2%NaOH) thermal conductivity and diffusivity increased by 18%. NBR is a polar rubber due to the presence of acrylonitrile group. When hydrophilic fibers are incorporated into a polar matrix like NBR the adhesion between matrix and fibers are stronger. This results in increased thermophysical properties.

Another observation is that NaOH concentration has an influence on the thermophysical properties of the composites. After steam explosion followed by treatment with NaOH (5%), the micro fibers are reinforced with NBR matrix. The 5% NaOH treated fiber composites showed higher thermal conductivity and diffusivity than macro fiber composites. Good
interfacial strength between fibril and rubber is the essential factor to achieve better reinforcement. The interfacial strength depends on surface topology of the micro fiber.

The NaOH treatment removes practically all non-cellulose components like waxy layer, lignin, etc. By the dissolution of lignin by alkali, some pores are formed on the fiber surface, which improves the contact area between the fiber and the matrix. Upon alkylation, the fiber diameter decreases and hence the aspect ratio increases. For the alkali treated composites, the moisture absorbing capacity of fibrils is reduced leading to improved wetting which produces a strong interfacial bond with the rubber matrix. Moreover, the treatment provides a number of small voids on the surface of fiber that promote mechanical interlocking between the fiber and the matrix. Since treated fibrils have more surface area, more cross-links will be produced within the rubber matrix leading to higher thermo physical properties. This may be due to the dissolution of alkali soluble fractions during alkali treatment.

When nitrile rubber is reinforced with HRH bonding agent, thermal conductivity and diffusivity values are higher compared to gum compound. This can be explained in terms of ionic bond formation between polar acrylo nitrile group and silanol groups of silica bonding agent. Chemical treatment has no major effect on the thermal properties of NBR-cellulose fiber composites. This is due to the fact that due to similar polarities we have a strong interphase in this system.
Table 5.10 Thermal conductivity, thermal diffusivity, specific heat and density of NBR/oil palm composites

<table>
<thead>
<tr>
<th>Material</th>
<th>k (W m⁻¹ K⁻¹)</th>
<th>a (m² s⁻¹) x 10⁻⁷</th>
<th>Cp (J kg⁻¹ K⁻¹)</th>
<th>ρ (kg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBR</td>
<td>0.133±0.001</td>
<td>0.546</td>
<td>2467±57</td>
<td>987±82</td>
</tr>
<tr>
<td>NBR+30phr macro fiber</td>
<td>0.162±0.001</td>
<td>0.706</td>
<td>2240±124</td>
<td>1024±112</td>
</tr>
<tr>
<td>NBR+30phr micro fiber</td>
<td>0.217±0.002</td>
<td>0.751</td>
<td>2685±72</td>
<td>1076±76</td>
</tr>
<tr>
<td>NBR+30phr microfiber+Resorcinol-hexa-hydrated silica</td>
<td>0.159±0.005</td>
<td>0.691</td>
<td>2069±92</td>
<td>1112±39</td>
</tr>
</tbody>
</table>

5.2.9 Comparison of dynamic properties of NR and NBR composites

Figure 4.45 represents the variation of storage modulus against temperature of micro fibril reinforced NR and NBR composites (30phr). It can be seen that E' increases at all temperatures in the case of NBR micro composites. The Tg values of NBR composites shifted to higher temperatures where as in the case of NR composites Tg values shifted to lower temperatures.

The variation of tanδ with temperature of oil palm micro fiber reinforced NR and NBR composites are shown in Fig. 4.46. As seen in the Figure micro fibril reinforced NBR composites possess lower damping capabilities than NR composites.
Figure 4.45  Storage modulus vs temperature of oil palm micro fiber/ NR and NBR composites (30phr)

Figure 4.46  Tanδ vs. temperature of oil palm micro fiber/NR and NBR composites (30phr)
5.3 Conclusions

The dynamic mechanical properties of NR ad NBR reinforced with macro/micro fibrils of oil palm fiber have been investigated. The storage modulus of the composites was found to increase with fiber loading because of the reinforcement imparted by the fillers. The unfilled compound has the highest tanδ value indicating a large degree of mobility and hence good damping characteristics. Addition of macro/micro fibers decreased the damping characteristics of composites, as the fibers acted as barriers to the free movement of the macromolecular chain. Incorporation of treated micro fibrils results in higher storage modulus, due to increased silane coupling cross-linking and formation of a strong fibril/matrix interface in the case of NR composites. The composites containing micro fibrils treated with silane coupling agent showed maximum dynamic properties. In the case of NBR reinforced treated microfiber composites, resorcinol-hexa-silica (HRH) bonding agent added composites gave better dynamic mechanical properties. The glass transition is shifted to the positive side up on the addition of treated micro fibers in both NR and NBR systems. It was found that incorporation of treated micro fibrils decreased the damping characteristics of the composite as the fibers acted as barriers to the free movement of the macromolecular chain. Increase of frequency is found to have a broadening effect on the tanδ curve. Activation energy for the glass transition of neat NR and NBR and the composites was calculated and found maximum for the treated micro fiber reinforced composites. The thermal degradation behaviour of oil palm fiber composites were analysed using thermogravimetric analysis (TGA). Addition of fibers resulted in an increase of thermal stability of both NR and NBR composites. The thermal stability of chemically modified fiber/ NR and NBR composites was better than untreated composites. The thermo physical properties of oil palm fiber
reinforced NR and NBR composites were studied. The incorporation of the oil palm fiber induces an increase of the effective thermal conductivity of the composites. This shows that thermal conductivity of composites is more important than NR or NBR matrix. The use of the theoretical series conduction model allowed estimating the transverse thermal conductivity of oil palm fibers composites. As we expected, the series model appears sufficient for the effective thermal conductivity estimation of this kind of composites. Using NaOH and HRH chemical treatment of fiber allow a significant increase of thermal conductivity, thermal diffusivity and density values of NR and NBR/oil palm micro composites in comparison with macro composites. This shows that the chemical treatment allows a better contact between the components (fiber/matrix) and reduces considerably the thermal contact resistance.

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