Chapter

8

THERMOGRAVIMETRIC AND DYNAMIC MECHANICAL ANALYSIS OF INTIMATELY MIXED SHORT SISAL/GLASS HYBRID FIBRE REINFORCED LOW DENSITY POLYETHYLENE COMPOSITES

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8.1. Introduction

The current trend of polymer scientists is to prepare thermoplastics and thermosetting composites of increased mechanical performance, light weight, low cost, covering different static and dynamic fields of application. By permutation and combination of various fibres and polymers, a wide range of composites which have unique properties for versatile applications, as successful alternatives to conventional materials like metals, wood, etc. have been prepared.

Thermal analysis is an important analytical method in understanding the structure-property relationship and mastering of the technology for molecular design and industrial production of different polymeric materials, especially fibre reinforced composites.

Moreover it is a useful technique to determine the thermal stability of the materials. It includes the determination of moisture and volatile components present in the composite. These components have a deteriorating effect on the properties of the composites. In the case of cellulose fibres, lignin degrades at a temperature around 200°C while other polysaccharides such as cellulose, at high temperatures. Most of the natural fibres lose their strength at about 160°C. Thermal studies of cellulose fibres and their pyrolytic behaviour is reported extensively in the literature. Kokta and Valde studied the effect of grafting of various polyacrylates on to cellulose and its influence on the temperature and heat of degradation using TG and DSC. The determination of filler content and its distribution analysis was carried out by Fuad et al. using thermogravimetric analysis. They observed good agreement and consistency between the actual filler content and filler content obtained by TG analysis.
Dynamic mechanical thermal analysis (DMTA) over a wide range of temperature provides valuable insight into the structure and viscoelastic behaviour of polymer composites. The dynamic properties are generally expressed in terms of storage modulus ($E'$), loss modulus ($E''$) and damping or loss factor ($\tan \delta$). The damping is a sensitive indicator of all kinds of molecular motions that are going on in a material during the testing. These dynamic parameters have been used to determine the glass transition temperature relation spectra, degree of crystallinity, molecular orientations, crosslinking, phase separation, structural changes resulting from processing and chemical composition of polymeric composites. Dynamic mechanical behaviour of unidirectional composites are dependent on both the volume fraction of fibres and the fibre orientation.

Dong and Gauvin applied DMTA analysis for the study of the interfacial region in carbon fibre reinforced epoxy resin composites. Among the various techniques for interface characterisation, DMTA has attracted ever more attention, because it provides sensitive and non destructive detection of the interfacial region. Akay observed that the presence of fibre reduces viscoelastic damping of carbon fibre/epoxy composites due to fibre-matrix interactions. Saha and Banerjee carried out a detailed study on the dynamic behaviour of unidirectional polyethylene/glass hybrid fibre reinforced polymethyl methacrylate composites. They observed that damping efficiency of the hybrid composites increased with increase in the relative volume fraction of polyethylene fibres.

Gassan and Bledzki studied the influence of surface treatment (MAH-PP) on the dynamic mechanical properties of natural fibre (jute) reinforced thermoplastics. They showed that maleic anhydride polypropylene (MAH-PP) copolymer increases the level of adhesion between polypropylene and jute fibre. Ghosh et al. reported the dynamic mechanical behaviour of jute/glass hybrid fibre reinforced polymer composites. Thomas et al. from the laboratory, conducted several detailed investigations of DMTA analysis in the field of natural fibre reinforced polymer composites.
As reported in literature,\textsuperscript{20} sisal fibre which has a medium damping efficiency, can be effectively used as a good reinforcement in LDPE, especially when low damping properties are required. However, the sisal fibre suffers from the serious disadvantage of poor thermal stability. On the other hand, glass has this advantage up to the required level. But its damping efficiency is relatively poor.\textsuperscript{9}

The main purpose of the present chapter is to evaluate the appropriate combination of sisal and glass performance in LDPE. This approach will be useful to obtain a good balance between the damping behaviour and thermal stability in the resulting hybrid composite material. The dynamic mechanical and thermal properties have been investigated. The dynamic mechanical and thermal properties have been investigated by varying the relative volume fraction of unidirectionally oriented fibres (sisal and glass) and fibre-matrix interfacial bonding.

8.2. Results and discussion

8.2.1 Thermogravimetric analysis

Thermogravimetric curves (TG) of low density polyethylene (LDPE), sisal fibre (SF), sisal reinforced LDPE (SRP), glass reinforced LDPE (GRP) and sisal/glass hybrid fibre reinforced LDPE (GSRP-50/50) are shown in Figure 8.1. The temperature range used for the analysis is 30-600°C. From Figure 8.1 it is observed that the degradation of LDPE starts at a temperature of 310°C while that of sisal fibre, below 150°C. The comparatively low thermal stability of the cellulosic component in the composite is clear from this observation. The dehydration of sisal fibre takes place at the temperature range of 60-110°C and above this temperature at about 200°C the degradation of the lignin in the fibre occurs. In general, it can be seen that the degradation of most of the cellulose takes place at a temperature of 350-400°C. It is also seen that the degradation of SRP takes place at a higher temperature than the sisal fibre. This confirms the fact that the thermal stability of sisal fibre is increased by the incorporation into
LDPE. It may be associated with good transmission of heat in SRP due to the interaction of sisal with LDPE matrix. In other words, localised heating effect is absent in SRP. It can be possible to enhance thermal stability of natural fibre reinforced composites by increasing the degree of interaction between fibre and matrix. Thermal stability of GSRP is found to be still higher than the thermal stability of SRP. It may be due to the high thermal stability of glass fibre compared to LDPE and sisal fibre. GRP shows highest thermal stability. Derivative thermogravimetric curves (DTG) (Figure 8.2) also supports this fact.

Figure 8.1. TG curves of (a) sisal fibre, (b) LDPE, (c) SRP (20% sisal), (d) GSRP (50/50 SRP/GRP) and (e) GRP (20% glass)
In DTG curves the peak observed at 65°C of sisal fibre corresponds to the heat of vapourisation of water from sisal fibre (Stage I). Physical desorption of water and intramolecular dehydration with concurrent formation of carboxyl and carbon-carbon double bonds of cellulose in sisal fibres takes place at the temperature range of 150-240°C. The breakdown of glucosidic linkage and cleavage of other C-O and C-C bonds in cellulose takes place at a temperature range of 240-400°C, or the second peak of sisal at about 350°C is due to the thermal depolymerisation of hemicellulose and the cleavage of the glucosidic linkage of cellulose (Stage II). The mechanism of the cleavage of glucosidic linkage is shown in Scheme 8.1.
The second peak of sisal, at about 350°C is due to the thermal depolymerisation of hemicellulose and the cleavage of the glucosidic linkage of cellulose (Stage II). The third peak at about 450°C of sisal may be due to the further breakage of decomposition products of Stage II, leading to the formation of char through levoglucosan. The mechanism of cellulose pyrolysis may be summarised as follows: (1) upon heating, cellulose undergoes several reactions leading to depolymerisation and char formation; (2) char products arise from repolymerisation of monomers or further thermal decomposition, or both; (3) anhydrides such as levoglucosan arise from depolymerisation and subsequent molecular rearrangement and (4) gaseous volatiles arise from decomposing residue or char. In the case of LDPE, major peak of DTG curve is observed at 400°C which indicates the degradation of saturated and unsaturated carbon atoms in polyethylene. The degradation mechanism of polyethylene is shown in Scheme 8.2. Polyethylene undergoes random degradation leading to the formation of fragments with active free radical ends. These may either undergo depolymerisation to form daughter free radicals and unsaturated compounds or undergo intramolecular transfer to form secondary free radical which again results in products similar to the earlier case. In the degradation pathway, further scission also can occur. In the case of SRP, three peaks were obtained, one major peak and two minor peaks. The minor peaks at 350 and 400 correspond to the degradation of cellulose and LDPE respectively. The major peak at 470°C corresponds to the

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\begin{align*}
\text{Cellulose} & \quad \text{Levoglucosan} \\
(1,6\text{-anhydro-}\beta\text{-D-glucose})
\end{align*}
\]

**Scheme 8.1. Mechanism of glucosidic linkages in cellulose**
degradation of dehydrocellulose. It is seen that in the case of SRP, the major peak is shifted to higher temperature region compared to sisal fibre and LDPE peak. The thermal stability of sisal fibre is enhanced in SRP due to the sisal-LDPE interaction. In the case of GSRP, thermal stability is again slightly increased as a result of the high thermal stability of glass fibre which acts as barriers to prevent the degradation of sisal. DTG curve of GRP shown in Figure 8.2 reveals that its thermal stability is higher than SRP and GSRP.

Scheme 8.2 Degradation mechanism of polyethylene
Step analysis of LDPE at thermogravimetric scan at 30-100°C shows a percentage mass drop of 1% whereas sisal fibre, SRP, GSRP and GRP show a mass drop of about 5, 3, 2 and 1% respectively. At 200°C, the mass drop of sisal fibre is 11%. It may be associated with the degradation of lignin from sisal fibre. Thermal decomposition of LDPE mainly starts at 250°C. At 300°C, the weight losses are 4, 19, 3, 2 and 1% for LDPE sisal, SRP, GSRP and GRP composites, respectively. At a temperature around 500°C, polyethylene is completely decomposed. Weight losses of LDPE, sisal fibre and composites at different temperatures are shown in Table 8.1. It can be understood that the stability of the composites is highest in GRP.

| Temperature (°C) | LDPE | Sisal | SRP (20% sisal) | GSRP (50/50 SRP/GRP) | GRP (20% glass) |
|-----------------|------|-------|-----------------|-----------------------|----------------
| 100             | 0    | 5     | 3               | 1                     | 0              |
| 200             | 1    | 11    | 3               | 2                     | 0              |
| 300             | 4    | 22    | 4               | 2                     | 1              |
| 400             | 50   | 65    | 20              | 5                     | 3              |
| 450             | 75   | 68    | 36              | 18                    | 7              |
| 500             | 100  | 79    | 68              | 58                    | 33             |

### 8.2.2 Dynamic mechanical analysis

Dynamic mechanical properties of fibre reinforced composites depend on the nature and distribution of the matrix materials and the reinforcing fibres, the
nature of the fibre-matrix interfaces and of the interfacial regions. Even a small change in the chemical and physical nature of the fibre for a given matrix and variations in relative compositions of the individual fibres and matrix may result in notable changes in the overall dynamic mechanical properties of the composite.

8.2.2.1 Effect of composition

Figure 8.3 shows that the storage modulus and mechanical loss factor of LDPE, SRP, GSRP (50/50 composition of sisal and glass) and GRP composites at a frequency of 10 Hz. It is seen that LDPE shows a minimum and GRP, a maximum storage modulus value. The increase in storage modulus follows the order: LDPE < SRP < GSRP < GRP. In all cases, the storage moduli ($E'$) decreases with increase of temperature. This indicates the loss in the stiffness of the material with increasing temperature. It can be further noted that the difference in storage moduli between each system increases at high temperature. This is because, at low temperature, fibres do not contribute much to imparting stiffness to the material. On increasing the temperature, the drop of matrix modulus is compensated by the fibre stiffness. It has been reported that in the case of carbon fibre reinforced nylon 66 composites, an increase in relative storage modulus value at all temperatures observed with increase in volume fraction of the fibre. This has been explained by the fact that the modulus of carbon fibre is not affected by changes in temperature. The high $E'$ value of GRP and GSRP compared to SRP indicates the presence of comparatively strong interaction between glass fibre and LDPE matrix than sisal and LDPE. Another reason is attributed to the high stiffness imparted by glass fibre compared to sisal fibre. The sharp decrease in storage modulus around a temperature of 110°C is due to the melting of composites. It is seen that LDPE starts melting at a temperature lower than 110°C. While all other systems melting at still higher temperature. GRP exhibits highest temperature for melting.
Mechanical loss factor (tan $\delta$) shown in Figure 8.3 shows a reverse trend from storage modulus. It is seen that tan $\delta$ value of LDPE decreases with the addition of fibres. The decrease is very much pronounced in GSRP and GRP composites due to the low damping efficiency of glass fibre. Ghosh et al. reported that the damping efficiency of jute fibre reinforced epoxy resin was substantially reduced by the hybridisation of jute with glass fibre. The overall decrease in tan $\delta$ of LDPE after the incorporation of fibres may be due to the higher elastic modulus of the fibres. In the case of LDPE the damping peak formed between 80 and 90°C is associated with melting of crystalline segments of polyethylene. However, in the case of SRP, GSRP and GRP the melting peak is shifted to high temperature region (110-120°C). This is associated with the decreased mobility of polyethylene chains by the addition of stiff fibres. The relaxation peak height of GSRP and GRP are higher than SRP, which is in contrary to the initial damping behaviour of composites at low temperature region. It may be due to the change in glass-PE interface in comparison with sisal-LDPE interface at higher temperature. The melting peak of GRP and GSRP is due to the high

Figure 8.3. Variation in storage modulus and loss factor (tan $\delta$) as a function of temperature at a frequency of 10 Hz.
stiffness of glass fibre compared to sisal fibre. In all the cases the overall damping behavior increases with temperature.

Figure 8.4 shows the effect of temperature on loss modulus ($E''$) of LDPE, SRP, GSRP (50/50) and GRP composites at frequency of 10 Hz. Loss modulus follows a similar trend as in the case of storage modulus.

![Figure 8.4. Variation in loss modulus as a function of temperature at a frequency of 10 Hz](image)

Figure 8.4 shows the variation of storage modulus and tan $\delta$ values of the hybrid composites (GSRP with sisal/glass composition 80/20, 50/50 and 20/80) at a frequency of 10 Hz containing untreated fibres as a function of temperature. In all cases, storage moduli ($E'$) decrease with increase of temperature. At any particular temperature, storage moduli slightly increase with increase in volume fraction glass fibre and decrease with increasing temperature. This is clearly evident from Figure 8.6. As the glass fibre content in the hybrid composite increases, the stiffness and hardness of the material increases, and consequently storage modulus also increases. It can be also noted that mechanical loss factor (tan $\delta$) of all the hybrid composite (Figure 8.5) increases with increase in temperature. The tan $\delta$ value of GSRP shows a slight decrease when the volume fraction of glass fibre...
increases. This is due to the higher inherent stiffness (modulus) character of E-glass and the consequent higher degree of stiffness of the composite.

![Graph](image)

Figure 8.5. Variation in storage modulus and loss factor (tan δ) as a function of temperature at a frequency of 10 Hz

![Graph](image)

Figure 8.6. Variation in storage modulus of GSRP (SRP/GRP) as a function of volume fraction of GRP at a frequency of 10 Hz
Figure 8.7 shows the effect of temperature on the loss moduli of hybrid composites at different sisal/glass composition and at a frequency of 10 Hz. As in the case of storage moduli, loss moduli of all the composites decrease with increasing temperature. It can also be noted that a slight increase in loss moduli is observed with increase in volume fraction of glass fibre.

8.2.2.2 Effect of chemical modifications

The chemical modification of fibre surface has great influence on the interface and hence on the dynamic mechanical properties of the hybrid composites. The influence of chemical modifications on the storage moduli of hybrid composites (GSRP) with 50/50 sisal/glass composition is shown in Figure 8.8. It is clear from the figure that a significant improvement in modulus is observed for treated fibre composite, which is attributed to the increase in interfacial stiffness resulting from the more intense fibre-matrix interaction.
Chemical modification improves the adhesion between fibre and matrix, resulting in lesser molecular mobility in the interfacial region. Introduction of functional group by the coupling agents enhances the fibre matrix adhesion resulting in lesser molecular mobility in the interfacial region. It is seen that the maximum improvement in storage modulus is observed in the case of silane treated composites. A detailed mechanism of fibre matrix interaction in chemically modified composites is given in Chapter 5. The effect of chemical modification on loss moduli is shown in Figure 8.9. Loss modulus also increases as a result of chemical modification. The storage and loss moduli increase in the order silane > BPO > KMnO₄ > DCP > stearic acid > untreated. The influence of chemical modification on tan δ of hybrid composite is shown in Figure 8.10. It is interesting to note that the melting peak of untreated composites is shifted to higher temperature region in treated composites. The damping of the BPO treated composites (at temperature >100°C) show highest value. At this temperature damping of treated composites decreases in the order: BPO > silane > KMnO₄ > DCP > stearic acid. In general damping decreases with all chemical modifications.

Figure 8.8. Variation in storage modulus of untreated and treated GSRP (50/50 SRP/GRP) as a function of temperature at a frequency of 10 Hz
Figure 8.9 Variation in loss modulus of untreated and treated GSRP (50/50 SRP/GRP) as a function of temperature at a frequency of 10 Hz

Figure 8.10 Variation in loss factor of untreated and treated GSRP (50/50 SRP/GRP) as a function of temperature at a frequency of 10 Hz
8.2.2.3 Effect of frequency

The viscoelastic properties of a material are not only dependent on temperature but also on the oscillating frequency at which the analysis is carried out. If a material is subjected to a constant stress, its elastic modulus will decrease over a period of time. It is due to that the material undergoes molecular rearrangement in an attempt to minimise the localised stresses. If the modulus measurements are performed at higher frequency over a short time, higher values of modulus will be obtained. On the other hand, if the reverse is done, it results in lower modulus values. On varying the oscillation frequency, changes occur in both $E'$ and $E''$ of untreated (Figure 8.11) and silane treated (Figure 8.12) GSRP (50/50) composites. At a particular temperature, the value of $E'$ tends to increase with frequency. It is due to the decreased mobility of LDPE chains at higher frequency. Similar plots for loss modulus ($E''$) also are presented in Figure 8.12. It can be seen that generally $E''$ decreases with temperature. Below 80°C $E''$ value decreases with increasing frequency while above this temperature a reverse trend is observed. The three dimensional damping peak of GSRP contains 50/50 SRP/GRP is shown in Figure 8.13. It is seen that damping increases with decrease of frequency.

![Figure 8.11](image)

**Figure 8.11.** Variation in $E'$ or $E''$ of untreated GSRP (50/50 SRP/GRP) as a function of temperature at different frequencies
Figure 8.12. Variation in $E'$ or $E''$ of silane treated GSRP (50/50 SRP/GRP) as a function of temperature at different frequencies

Figure 8.13. Three dimensional curve of untreated GSRP (50/50 SRP/GRP)

The variation in mechanical loss factor of LDPE, SRP, GSRP (50/50) and GRP composites as a function of frequency at a temperature of 85°C is shown in Figure 8.14. It is seen that in all cases, the tan $\delta$ value decreases with frequency at the above mentioned temperature. It is also seen that tan $\delta$ values of all systems come closer at high frequency than at low frequency.
The viscoelastic properties at a given frequency $f$ is quantitatively equivalent to those of an experiment carried out over a time $t = 1/2\pi f$. It is already noted that the time and temperature have essentially equivalent effects on the modulus value of polymers. Figure 8.15 shows the variation of $E'$ of untreated GSRP (50/50) at different temperatures as a function of log $t$. The distance between the curves shown in Figure 8.15 gives the value of the shift factor ($\alpha_T$). Shift factors were calculated by displacing the $E'$ versus log $t$ curves vertically and horizontally. Using these shift factors at different temperatures master curves can be plotted. The temperature of $80^\circ C$ was taken as the reference temperature in constructing the master curve. The master curve of untreated GSRP (50/50) is shown in Figure 8.16. Using this master curve it is possible to predict the viscoelastic behaviour of a material well outside the frequency or time range of mechanical equipment.
Figure 8.15. $E'$ vs. log $t$ curves of GSRP (50/50 SRP/GRO) composites for temperatures from 40-110°C

Figure 8.16. Plot of $\log E' \times a_t$ vs. log $t$
Figure 8.17 shows plot of loss modulus ($E''$) versus storage modulus ($E'$) of SRP, GRP and GSRP (50/50) composites. This analysis is called Cole-Cole analysis and the resulting plots are called Cole-Cole plots. The viscoelastic properties of the composites can be explained using Cole-Cole plots. According to Cole-Cole analysis a purely homogeneous system shows a perfect semicircular curve while two phase systems show two modified semicircles. Figures 8.17 and 8.18 show the Cole-Cole plots of untreated SRP, GRP, GSRP, silane and BPO treated GSRP with 50/50 sisal/glass composition. The curves indicate that the system is macroscopically heterogeneous.
Figure 8.18. Cole-Cole plots of untreated, silane and benzoyl peroxide treated GSRP (50/50 SRP/GRP) composites

8.3. References


