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Elastic and viscoelastic properties of sugarcane bagasse-filled poly(vinyl chloride) composites

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Abstract Elastic and viscoelastic properties of sugarcane bagasse-filled poly(vinyl chloride) were determined by means of three-point bending flexural tests and dynamic mechanical and thermal analysis. The elastic modulus, storage modulus, loss modulus, and damping parameter of the composites at fibre contents of 10, 20, 30, and 40% in mass were determined, as well as those of the unfilled matrix. There was a correlation between the elastic modulus and storage modulus of the composites. Moreover, the elastic and viscoelastic properties of the composites were highly influenced by fibre content.

Keywords Bagasse · Composite · Elasticity · Viscoelasticity · Thermomechanical

Introduction

In the past few decades, the development of new materials that involve natural resources as the raw material, especially as a composite material, has accelerated. Both the properties and cost of various natural fibres and their composites have been evaluated to determine their potential to replace glass fibre-reinforced plastic composites in some applications. Compared to glass fibre, the advantages of natural fibres include their low cost, low energy consumption, zero CO_2 emission, low abrasive properties, low density, high resistance to crack propagation, non-toxicity, and their continuous availability [1–3].

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One of natural fibres with high availability is sugarcane bagasse, a residue of the sugarcane milling process. In Malaysia, the annual production of sugarcane reaches a million tonnes, which is less than 0.1% of the world annual production [4]. Nearly 30% of that number will turn into bagasse when it is crushed in a sugar factory. This procedure produces a large volume of bagasse wastes that may have an extremely harmful effect upon the environment if not suitably treated [5, 6]. Moreover, the stock is abundant, and the price of sugarcane bagasse is less expensive than that of other natural fibres [6].

The matrix selected in this study was poly(vinyl chloride) (PVC). It is one of the most well-known and the least expensive thermoplastic polymers. This thermoplastic is used in a broad range of applications, and its use has grown rapidly. The advantages of this material include ease of fabrication and long life. It exhibits good mechanical and chemical properties and can be used in a wide range of corrosive fluid environments. Furthermore, the properties of PVC can be customised by the addition of plasticisers and other additives for production of a rigid or flexible product [7, 8]. Many researchers have investigated the properties of PVC-filled natural fibre composites. So far, there are at least nine variants of natural fibres that have been studied for filler/reinforced materials: wood, bamboo, pine, rice straw, sisal, oil palm, banana, coconut, and sugarcane bagasse [9–21]. However, the dynamic mechanical and thermal analysis (DMTA) of natural fibre-filled PVC, especially sugarcane bagasse-filled PVC, has not been widely discussed.

In this study, elastic and viscoelastic properties of sugarcane bagasse-filled PVC composites were determined by means of three-point bending flexural tests and DMTA. The static and dynamic flexural behaviour of unfilled PVC and the sugarcane bagasse-filled PVC were examined in various fibre loadings (10, 20, 30, and 40%).

Experimental

Figure 1 shows the flow chart of the experiment. In general, the experiment was divided into three processing steps: materials preparation, composite fabrication, and materials characterisation.

Materials

The matrix used in this study was poly(vinyl chloride) compound PVC IR045A supplied by Polymer Resources Sdn. Bhd., Kelang, Selangor, Malaysia. This compound consists of a PVC resin, processing aids, lubricant, and some additives designed for general purpose application.

The sugarcane bagasse fibre studied was a residue of the sugarcane milling process obtained from a traditional sugarcane juice maker in Malaysia. The stalk of the sugarcane plant was divided into two parts: outer rind and inner pith. The effect of different fibre sources (pith and rind) was observed, as well as the effect of fibre content on the modulus of elasticity and viscoelastic behaviour of the composites.

Preparation of composites

Both the pith and rind of sugarcane bagasse were sun-dried for 2 × 12 h before they were fed into a ring knife flaker separately to obtain short fibres (below 3 cm in length). The fibres were then sieved to obtain more homogeneous dimensions, followed by oven-drying at 80 °C for 24 h. The 40 mesh of fibres were used in this study.

A thermal mixing process was carried out using a Haake Polydrive R600 internal mixer at a temperature of 170 °C and a rotor speed of 50 rpm. PVC pellets were fed into the chamber and mixed for 5 min, followed by feeding of the fibres. The total mixing time was 15 min. In this study, 10, 20, 30, and 40% mass fractions of pith and rind fibres were prepared.

The final stage of the composite preparation process in this study was hot-pressing. Hot-pressing was carried out at a temperature of 170 °C for 12.5 min, and the mixture was then cooled under pressure to room temperature. The final products were in the form of plates with dimensions of 15 cm × 15 cm × 3 mm. The plates were then cut into a rectangular shape with dimensions of 13 cm × 1.3 cm × 3 mm and 5.5 cm × 1.3 cm × 3 mm for static flexural and DMTA measurements, respectively.

Materials testing

A three-point bending flexural test was conducted using an Instron 3365 machine with a span length of 10 cm at a crosshead-speed of 2 mm min^{-1}. The modulus of elasticity was calculated from the formula represented in Eq. 1.

$$E = \frac{L^3 m}{4bd^3} \quad (1)$$

where L, b, d, and m are the span length, the width of the test specimen, the depth of the span, and the slope of the tangent to the initial straight line portion of the load–displacement curve, respectively.

Meanwhile, DMTA measurements were executed on TA Instruments DMA Q800 equipment operating in a dual cantilever bending mode at 1 Hz in frequency with a span length of 5 cm. Each specimen was heated at the rate of 10 °C min^{-1} from 25 to 120 °C. The storage modulus (E'), loss modulus (E''), and tan δ (E''/E') were measured as a function of temperature.

Results and discussion

The effects of filler on the elastic modulus

The elastic moduli of both pith/PVC and rind/PVC composites, in general, were observed to increase with the

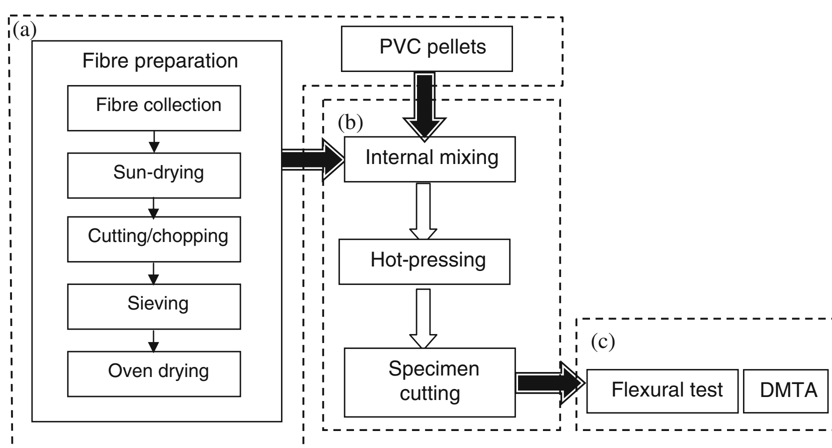

Fig. 1 Flow chart of the experiment includes (*a*) materials preparation, (*b*) composite fabrication, and (*c*) materials characterisation

increase of fibre content (see Fig. 2). It is well known that cellulose is of higher elastic modulus compared to thermoplastics, including PVC. Hence, the incorporation of fibre into the matrix increases the elastic modulus. In addition, the elastic modulus of rind/PVC was superior compared to pith/PVC composites at the same fibre content. It is reported that the rind component consists of a higher ratio of cellulose component compared to the pith component [22]. As a result, the rind offers better mechanical properties than pith.

The low value of the elastic modulus at low fibre contents (10 and 20% for pith/PVC and 10% for rind/PVC) can be explained by the fact that there was a reduction in the effective cross-sectional area, which is the area that participates in the transfer of the loading stresses. The loading stress can be transferred completely only if there is perfect adhesion between the fibre and matrix. In the absence of adhesion, the interphase layer between the fibre and matrix is not able to transfer the stress [23]. In the actual case, the quality of adhesion between matrix and fibre varies, ranging from poor (almost no adhesion) to excellent (almost perfect adhesion). This quality of adhesion affects the effective cross-sectional area; a better quality of adhesion results in a higher effective cross-sectional area. At low fibre content, the amount of fibres was enough to increase the elastic modulus of the system, whilst the reduction of cross-sectional area occurred, resulting in low elastic modulus. However, the effect of reduction of cross-section area was less dominant when the amount of fibres increased, resulting in higher elastic modulus of the system.

The effects of filler on storage modulus

The storage modulus at elevated temperatures of the pith/PVC and rind/PVC composites of various fibre contents is depicted in Figs. 3 and 4. There was a correlation between the storage modulus at the initial temperature (25 °C) and the modulus of elasticity obtained from the static bending test. Similar to the modulus of elasticity, the storage modulus of the composites with low fibre contents (10 and 20% for pith/PVC and 10% for rind/PVC) was found to be lower than that of unfilled PVC. The storage modulus of the composites, however, increased with increasing fibre content. At higher fibre contents (30 and 40%), the storage moduli of the composites were higher than that of unfilled PVC. The correlation between the storage modulus and the modulus of elasticity is in agreement with the results for the static and dynamic moduli of jute/vinylester composites reported by Ray et al. [24]. Hence, the trend of the storage modulus at the initial temperature also represents the trend of the static modulus of elasticity of the composites.

It is observed that the storage modulus decreased at elevated temperatures. Moreover, a large decrease in the modulus was observed at a range of temperatures between 70 and 90 °C, which indicates a glassy–rubbery transformation. Furthermore, it is also observed that the curves of pith/PVC were shifted to the right as the fibre content increased, showing that the incorporation of fibre increased the thermal stability of the PVC. The storage modulus of the filled systems, including the low fibre content, above T_g was higher compared to that of unfilled PVC, indicating the higher temperature stability of the composites.

Different results were observed in rind/PVC composites. Figure 4 shows that the curves of rind/PVC composites were shifted to the left as the fibre content increased up to 30% and then returned to the right at a fibre content of 40%. This result indicates that the thermal stability of the composite decreased with increasing fibre content up to 30% and then increased when the fibre content increased to 40%. Hence, amongst the four types of fibre content, 40% is the most effective fibre content to improve the thermal stability of rind/PVC composites.

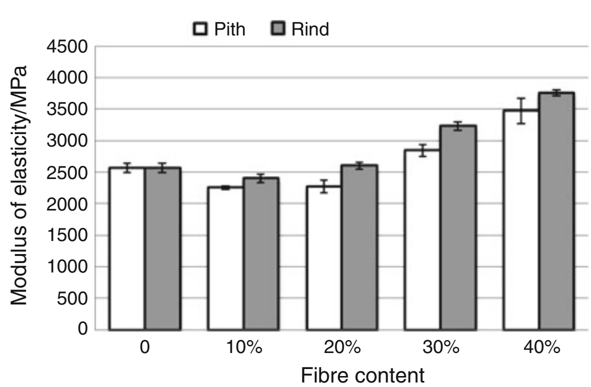

Fig. 2 Modulus of elasticity of pith/PVC and rind/PVC composites

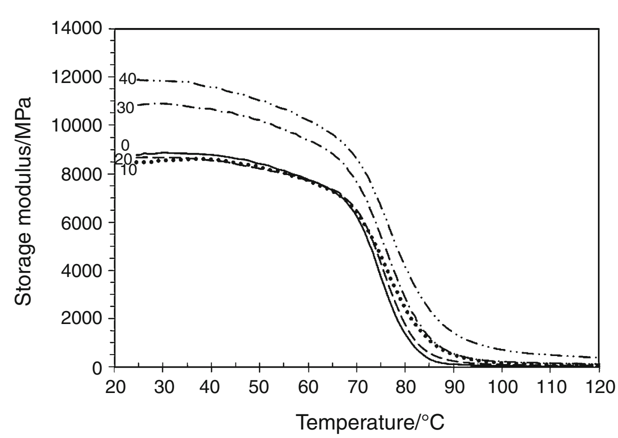

Fig. 3 Storage modulus of pith/PVC composites

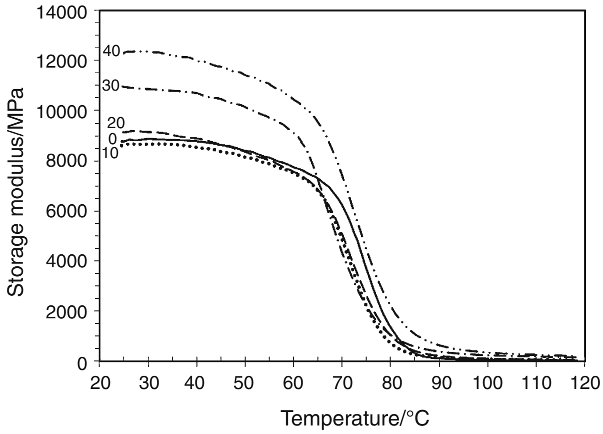

Fig. 4 Storage modulus of rind/PVC composites

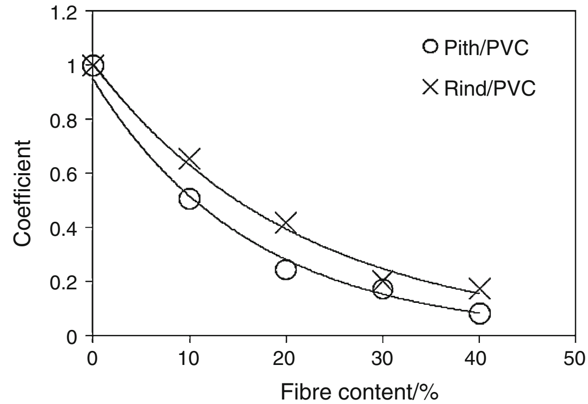

Fig. 5 The variation of the filler effectiveness coefficient with fibre content

In addition, the storage modulus of both the glassy and rubbery regions can be used for calculating the C coefficient, which represents the effectiveness of fillers on the modulus of the composites [25].

$$C = \frac{\left(E'_{\mathrm{G}}/E'_{\mathrm{R}}\right)_{\mathrm{composite}}}{\left(E'_{\mathrm{G}}/E'_{\mathrm{R}}\right)_{\mathrm{matrix}}} \quad (2)$$

where E'_{G} and E'_{R} are the values of the storage modulus in the glassy and rubbery regions, respectively. Higher values of the constant C represent the lower effectiveness of the filler. The measured E' values at 60 and 100 °C were used as E'_{G} and E'_{R}, respectively. The values of C obtained for various fibre contents are represented in Fig. 5, where it can be seen that the coefficients of both the pith/PVC and rind/PVC composites decreased exponentially with increasing fibre content. In other words, the effectiveness of the filler increased with the increase in the fibre content up to a fibre content of 40%, indicating that the fibres embedded in the viscoelastic system successfully reduced the mobility and deformability of the matrix. Moreover, the coefficient of rind/PVC was higher than that of pith/PVC composites, indicating that pith was more effective in reducing the mobility and deformability of PVC compared to rind.

The effect of filler on the loss modulus

The loss modulus, E'', is defined as the ratio of stress to strain when the stress is 90° out phase with the strain and is expressed in Eq. 3:

$$E'' = \frac{\sigma_0}{\varepsilon_0} \sin \delta \quad (3)$$

where σ_0, ε_0, and δ_0 are the maximum stress, the strain at maximum stress, and the difference between the applied stress and resultant strain, respectively. The loss modulus

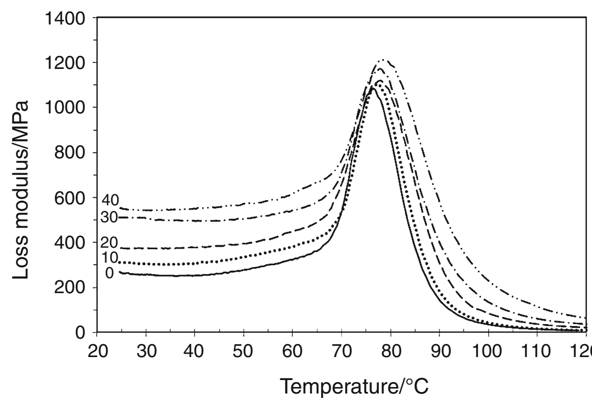

Fig. 6 Loss modulus of pith/PVC composites

measures the viscous response of material, which is the energy lost or dissipated when the material is deformed [25]. The viscous response of the pith/PVC and rind/PVC are represented in Figs. 6 and 7, respectively. Both curves show that there is a loss modulus peak for each fibre content of the composites, which is attributed to the mobility of the matrix molecules [24]. The maximum of loss modulus was reached as the storage modulus decreased because of the free movement in the polymeric chain at higher temperatures [26]. The peak of pith/PVC loss modulus, which is also considered the glass transition temperature, T_{g}, shifted to the higher temperature when the fibre content increased. The polymer molecules near the surface of the pith were immobilised due to various molecular interactions, which increased the T_{g} of the composites.

A different trend was found for the rind/PVC composites compared to the pith/PVC composites. Whilst the T_{g} of the pith/PVC composites increased with increasing fibre content, the T_{g} of the rind/PVC performed otherwise up to

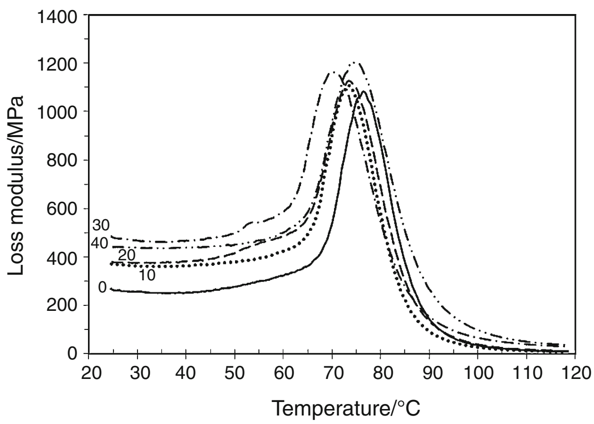

Fig. 7 Loss modulus of rind/PVC composites

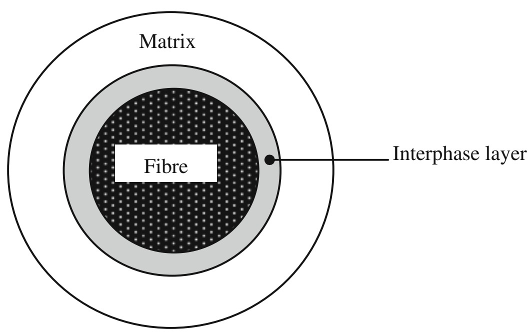

Fig. 8 Schematic diagram shows the fibre, matrix, and interface layer

a fibre content of 30%. The increase of T_g was only obtained at a fibre content of 40%; however, the value was still lower than that of unfilled PVC. It seems that the addition of rind was less effective in immobilising the PVC molecules near the surface of the rind at a particular temperature due to the lack of molecular interaction between the rind and PVC, especially at a low fibre content. The surface interaction was observed to be better at a fibre content of 40%. However, it was not good enough to increase the T_g of the system.

Another valuable object to observe is the width of the peak, which indicates the quantity of the fibre–matrix interaction. When a fibre is incorporated to a polymer matrix, there is an interaction between the fibre and matrix that generates a difference in the physical state of the matrix surrounding the fibres, called the interphase layer [25]. A schematic diagram of the fibre, matrix, and interphase layer is shown in Fig. 8. The volume of the interphase layer, which is not present in the unfilled matrix, may cause an additional transition, resulting in broader glass transition behaviour. A greater volume in the interphase layer causes a greater width of the loss modulus peak.

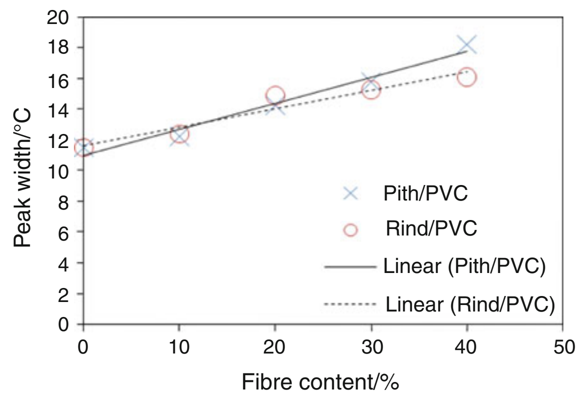

Fig. 9 The variation of peak width of loss modulus with fibre content

The increase of the peak width at the half height of the loss modulus corresponding to increasing the fibre content up to 40% is depicted in Fig. 9. This figure shows the increase of the interphase layer volume as the fibre content was increased. Moreover, it also indicates that the fibres were distributed well and that the optimum condition was not reached at a fibre content of 40%. When the fibre content is beyond the optimum condition, the peak width of the loss modulus decreases as a consequence of fibre agglomeration and an increase in fibre to fibre contact [27]. It seems that there is no significant difference between pith/PVC and rind/PVC composites in terms of the loss modulus width. It should be noted that the increased width of the peak in the loss modulus curve was a result of quantity (volume) of the interphase layer instead of its quality, such as the strength of fibre–matrix adhesion.

The effects of filler on the damping parameter

The damping parameter, tan δ, is the ratio of the loss modulus to the storage modulus. It is a dimensionless property that is related to the ability of a material to absorb vibrational energy. Whilst the storage and loss moduli indicate elastic and viscous responses, the damping parameter is an indicator of the viscoelastic response of a material. Like the peak of the loss modulus curve, the damping peak occurs in the region of the glass transition where the material transforms from a rigid (glassy) state to a more elastic (rubbery) state and can be used to assign the T_g [26]. The value, however, may be different [24]. Hence, it is important to write which peak was used when reporting the T_g.

Figures 10 and 11 represent the damping parameter curves of pith/PVC and rind/PVC composites, respectively. It can be clearly observed that the height of the peak of both composites decreased with increasing fibre content. In

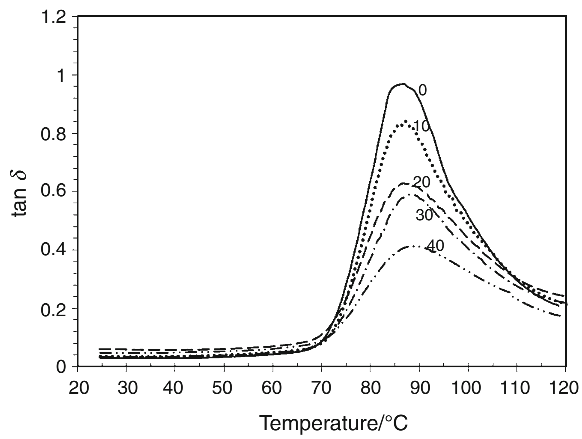

Fig. 10 Damping parameter of pith/PVC composites

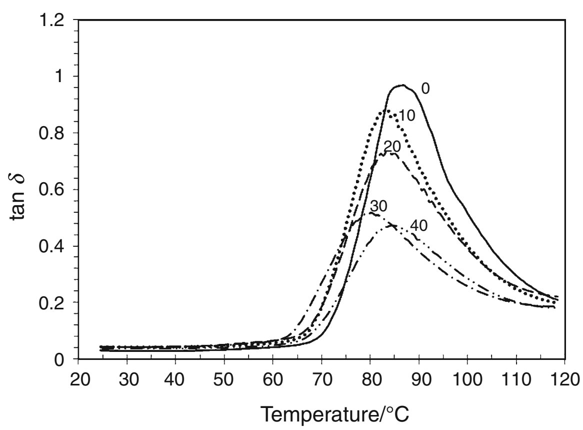

Fig. 11 Damping parameter of rind/PVC composites

a composite system, the composition of the materials greatly affects the damping parameter. When the elastic fibre is incorporated, the system is more elastic. As the damping parameter is the ratio of the viscous and elastic responses, it decreases with increasing content of the elastic substance.

Moreover, it is observed that the trend of T_g based on tan δ shows an agreement with the trend of T_g based on the loss modulus. The values of T_g obtained from tan δ curve, however, were higher than those obtained from the loss modulus curve. The peaks of the damping parameter were located at a temperature of more than 80 °C (Fig. 10), whilst the peaks of the loss modulus were located at a temperature less than 80 °C (Fig. 6).

Conclusions

The elastic and viscoelastic properties of sugarcane bagasse-filled PVC composites are greatly affected by the fibre source and fibre content. Incorporation of a low fibre content of pith or rind into PVC decreases elastic properties by means of the modulus of elasticity and the storage modulus of PVC at the initial temperature. However, the elastic properties of composites increase with increasing fibre content. Increasing the fibre content may increase the effectiveness of the filler on the elastic and storage moduli. In addition, the rind/PVC composites offer superior elastic response compared to pith/PVC composites. The pith/PVC composites, however, offer better thermal stability and interfacial bonding compared to rind/PVC composites. In terms of viscoelastic properties, it is observed that the incorporation of fibres decreases the damping parameter of the composites.

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