CHEMICAL MODIFICATION OF FLAX REINFORCED POLYPROPYLENE COMPOSITES

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Abstract

This paper presents an experimental study on the static and dynamic mechanical properties of nonwoven based flax fibre reinforced polypropylene composites. The effect of zein modification on flax fibres is also reported. Flax nonwovens were treated with zein coupling agent, which is a protein extracted from corn. Composites were prepared using nonwovens treated with zein solution. The tensile, flexural and impact properties of these composites were analysed and the reinforcing properties of the chemically treated composites were compared with that of untreated composites. Composites containing chemically modified flax fibres were found to possess improved mechanical properties. The viscoelastic properties of composites at different frequencies were investigated. The storage modulus of composites was found to increase with fibre content while damping properties registered a decrease. Zein coating was found to increase the storage modulus due to enhanced interfacial adhesion. The fracture mechanism of treated and untreated flax reinforced polypropylene composites was also investigated from scanning electron microscopic studies.

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1. INTRODUCTION

The application of natural fibres is being targeted in various fields due to both environmental and economical benefits. Natural fibres are renewable, biodegradable, safe to use and the most important reason being its high specific strength to weight ratio. This is of special significance in transportation applications as it leads to weight reductions and thus savings in fuel consumption. Among all the natural fibres, flax is considered to be one of the strongest and easily available. The tensile strength of elementary flax fibres is found to be in the region of 1500MPa[1].

The advantages of using polypropylene as matrix are their relatively low processing temperature which is essential because of low thermal stability of natural fibres and their good properties and lower cost. Nonwovens are one of the products popularly used as reinforcements in composites for many applications since they possess a good combination of strength, lightweight, and flexibility compared to conventional materials[2].

Natural fibres are hydrophilic in nature as they are lignocellulosic, which contain strongly polarized hydroxyl groups. These fibres, therefore, are inherently incompatible with hydrophobic thermoplastics, such as polyolefins. The major limitations of using these fibres as reinforcements in such matrices include poor interfacial adhesion between polar-hydrophilic fibres and non polar-hydrophobic matrix, and difficulties in mixing due to poor wetting of the fibres with the matrix. Therefore, it is imperative that natural fibres should be subjected to chemical modification to increase the compatibility and adhesion between fibres and matrix[34].

It would also be desirable that the chemical used for the modification of natural fibres preserves the biodegradable nature of natural fibres. Ideally, the chemicals used for modification should also be from renewable resources. In this study, we have attempted to use zein as a coating on natural fibres to see if it influences the interfacial mechanism between fibre and matrix. Zein is a natural protein derived from corn and is composed of mainly amino acids and glutamic acid, leucine and alanine. Zein

forms tough coatings and is resistant to microbial attack and possesses the additional benefits of being renewable and biodegradable.

Researchers[5] have reported studies on the properties of composites from hemp nonwovens mats and polyester resin. The authors observed that mechanical properties were found to be maximum at a fibre loading of 30 %. Hill et al[6] investigated the effect of environmental exposure on the properties of coir and oil palm mats reinforced polyester composites. They observed that composites containing acetylated fibres were more resistant to biodegradation.

Recently Kim[7] reported studies on the processing and properties of gluten-zein composites. The author observed the compressive yield strength of the composites to be around 40 MPa which was comparable to that of polypropylene. In another interesting study, Beckermann and Pickering[8] investigated the properties of hemp fibre reinforced polypropylene composites after alkali treatment. It was found that injection moulded hemp fibre reinforced polypropylene composite consisting of 40 wt% NaOH/Na_2SO_3 treated fibre, 4% MAPP and polypropylene had the highest tensile strength (50.5 MPa) and Young's modulus (5.31 GPa) of all the composites studied.

Although there have been many studies on lignocellulosic short fibre composites, only a few mention the use of nonwovens as reinforcement in composites. The biggest advantage of this type of composite is their low processing cost, combined with their ecological and technological benefits. This study attempts to investigate the static and dynamic mechanical performance of reinforced polypropylene composites with flax nonwoven. The effect of zein coating on nonwovens is also analysed in terms of properties of composites.

2. EXPERIMENTAL

2.1 Materials

South African flax line fibres were cottonised on Temafa Cottonization line by processing flax fibres through 1 pass Lomy (at speed 680 rpm) and 1 pass Cottonizer (at 1470 rpm) to produce needle-punched nonwovens. The needle-punched nonwovens from 100% cottonised flax fibres with an area weight of 200 g/m² was

used in this study. Polypropylene in sheet form (6 mm thickness), with a density of 0.9g/cc and melt flow index of 1.5g /10 min was procured from Ampaglas SA. Zein was obtained from Scientific Polymer Product Company, Ontario, NY. All other chemical reagents used in this study were of analytical grade.

2.2 Preparation of composites

Composites were prepared from nonwoven flax and polypropylene on the basis of varying fibre content. The flax nonwoven mats were cut into small uniform squares (30 cm x 30 cm) and then dried in an air oven at the temperature of 110°C for 7 h. The dried nonwoven mats were placed between weighed polypropylene sheets. This was wrapped in Teflon® sheets and sandwiched between two aluminium plates. These two plates were then placed between the two platens of compression moulding press and cured at a pressure of about 35 bar for 20 minutes at 210°C, followed by cooling under pressure for 3 minutes.

3.0 Analysis

Tensile and three-point bending tests were carried out using an Instron Universal Testing Machine, model 3369. Tensile testing on rectangular specimens was measured according to ASTM methods D638 at a crosshead speed of 50 mm/min and a gage length of 50 mm Flexural testing was carried out in accordance with ASTM D-790, at a crosshead speed of 5mm/min and a span length of 60 mm.

Charpy impact strength was measured on an Instron Dynatup, according to ASTM D256, using notched samples. Following test conditions have been used; span length 80 mm and drop weight 6.39 kg. During impact, resistive force exerted by the sample on the striker was measured as a function of time.

Five specimens were tested for each test and the average data have been reported.

Dynamic mechanical analysis was carried out using the Perkin Elmer DMA 8000. Samples of dimensions 50 x 12 x 3 mm were used for testing. The testing temperature ranged from -20°C to 150°C and the experiment was carried out at frequencies 0.1,1,10 and 100 Hz. The samples were tested under dual cantilever mode at strain amplitude of 0.05mm.

Scanning electron microscopic studies were conducted using Philips XL 30 SEM to analyse the fracture behaviour of the composites. The fracture ends of the tensile

specimens were mounted on aluminium stubs and gold coated to avoid electrical charging during examination.

4. Results and Discussion

4.1. Effect of fibre content

Figures 1 presents the variation in tensile strength and modulus with fibre weight fraction, respectively. It can be seen that as fibre content increases, the tensile strength of composites also increases. This shows that the incorporation of flax fibres leads to uniform and effective stress transfer within the composite. The modulus which is an indication of load bearing capacity also increases with fibre weight fraction. Tensile modulus is mainly dependent on fibre volume fraction and not on physical structure of fibres[9].

Flexural strength is a combination of the tensile and compressive strengths, which directly varies with the interlaminar shear strength. In flexural testing, various mechanisms, such as tension, compression and shearing take place simultaneously. The flexural strength and modulus of different composites are compared in Figure 2 and in general, both are seen to increase with the increase in the fibre content. The increase in flexural strength is small for the fibre weight fraction of 20%, thereafter the increase at 30% is higher but a pronounced increase occur at 40% fibre weight fraction. Similarly a noticeable improvement is observed in the flexural modulus at 40% fibre weight fraction.

Impact strength is the ability of a material to resist the fracture under applied stress at high speed. The impact properties of the composite are directly related to its overall toughness but the impact energy measured here is only for relative comparison and does not give accurate toughness of the material. The fibres play a very important role in the impact resistance of the composite as they interact with the crack formation in the matrix and act as stress transferring medium. The variation of impact strength with fibre loading is shown in Figure 3.

It can be seen that impact strength increases, reaches its maximum at 30% weight fraction of fibres and then decreases at 40%. The energy dissipation mechanisms

operating during impact fracture are matrix and fibre fracture, fibre–matrix debonding and fibre pull out. Fibre fracture dissipates lesser energy compared to fibre pull out and is the common mechanism of fracture in fibre reinforced composites. As the main failure mechanism in these composites is fibre pull out, impact strength increases with fibre loading. At higher fibre loadings the friction between the fibres may also contribute to the fracture process. This results in lower energy dissipation and hence impact strength decreases.

5. Chemical Modification of Nonwovens

5.1 Zein modification of flax nonwovens

Zein belongs to the characteristic class of proteins known as prolamines which occur specifically in cereals. The protein products from corn wet milling are corn gluten meal (CGM) and corn gluten feed (CGF) and zein is obtained as a by-product from corn gluten meal[10,11,12].

2 % of zein solution was prepared by mixing with an ethanol/water mixture in the ratio 80/20. The flax nonwovens were immersed in this solution and were allowed to stand for 2 hours. The ethanol/water mixture was drained out and the nonwoven was dried in air and then in an oven at 110°C until completely dry. These modified nonwovens were used to prepare the composites.

5.2 Effect of zein modification

Figure 4 exhibits the tensile and flexural properties of untreated and zein modified composites. It can be seen that after modification there is substantial increase in tensile and flexural strength. Tensile strength increased by 14% while flexural strength registered almost two-fold increase. This suggests that there has been better interfacial bonding between fibres and matrix. However, the impact strength is seen to decrease with zein protein modification. This decrease in impact strength is generally explained by assuming that as the fibre-matrix adhesion improves, the slippage of fibres from the matrix becomes difficult and the fibre breakage becomes a dominant mode of failure mechanism. As fibre breakage results in lower energy dissipation, impact strength also decreases.

Zein is neither soluble in pure water nor in alcohol but requires a high percentage of alcohol-aqueous system for dispersion There are mainly four types of zein (α,β,χ,δ) which are classified according to their solubility properties. The isoform α-zein, which accounts for ~85% of zein in the corn kernel, has a unique amino acid sequence containing more than 50% nonpolar amino acids. The secondary and tertiary structure of zein was reported as having a possible configuration containing 9 or 10 α-helix segments folded upon each other in a nonparallel fashion. According to that model, helical segments are arranged in a ring of "pencils" held together, side-by-side, by hydrogen bonds and linked at each end by glutamine-rich turns or loops. The exterior of the helical segments forming the lateral faces have a hydrophobic character, whereas the top and bottom surfaces containing the glutamine-rich loops are hydrophilic[13]. Therefore, zein is amphiphilic in nature having affinity for both polar and non-polar groups. This characteristic allows it to bind itself between the polar flax nonwovens and non-polar matrix results in enhanced mechanical properties. A schematic sketch showing the interaction between flax fibres, zein and polypropylene is presented in Figure 5.

5.3 Scanning electron microscopic studies

Scanning electron microscopy is a common method to analyze the level of fibre/ matrix adhesion. Enormous amount of studies has been conducted to evaluate the bonding between matrix and fibre. Analysis of the morphological features of fracture surfaces by SEM is an important tool for observing the surface morphology of fibres, the cause of crack initiation and the failure process in composites. Figure 6(a) shows the tensile fractured surface of untreated flax nonwoven composite at 30%. The presence of cavities is clearly visible. This indicates that the level of adhesion between the fibres and the matrix is poor and when stress is applied it causes the fibres to be easily pulled out from the matrix, leaving behind gaping holes. Figure 6(b) shows the tensile fracture surface of zein treated flax nonwoven composite at the same fibre loading. The figure shows the presence of a number of short broken fibres projecting out of the polypropylene matrix indicating that zein modification definitely improves the bonding between the fibres and matrix.

5.4 Dynamic mechanical analysis

Dynamic mechanical analysis is a very useful technique for investigating the mechanical behavior of a material based on its viscoelasticity. A dynamic mechanical test measures the response of a material as it is deformed by a sinusoidal or other periodic stress. The dynamic mechanical properties of a composite material depend on the fibre content, presence of the additives like fillers, compatabiliser, fibre orientation and the mode of testing. Natural fibre reinforced polymers are used to a great extent for the interior lining of cars and commercial vehicles. For these applications, the strength and stiffness properties have to satisfy the requirements of low temperatures at about –20°C and higher temperatures of up to 100°C. For establishing such a wide range of temperature-dependent material data, dynamical mechanical analysis is essential.

5.4.1 Effect of fibre loading

5.4.1.1 Storage Modulus

Storage modulus (E') provides valuable input into the stiffness of composites. The variation of storage modulus with temperature at different fibre loading at 1 Hz is given in Figure 7. It can be seen that storage modulus increases with increasing flax content at all temperatures when compared to the polypropylene. When fibres are incorporated in the polypropylene matrix, the stiffness of the composite increases resulting in high storage modulus. Also, the addition of fibres allows effective stress transfer at the interface, which consequently increases the storage modulus.

5.4.1.2 Loss Modulus

Loss modulus (E") measures the viscous response of materials and is related to amount of energy lost. The variation of loss modulus with temperature at different fibre loading is shown in Figure 8. It can be seen that loss modulus increases with the increase in fibre loading and reaches a maximum and then decreases. The maximum heat dissipation occurs at the temperature where the loss modulus is maximum indicating a relaxation phenomenon. The increase in loss modulus is attributed to the increase in energy absorption caused by the addition of fibres.

5.4.1.3 Mechanical damping factor (tan δ)

Damping is an important parameter related to the study of dynamic behaviour of fibre reinforced composite material. The major contribution to damping in composite is due to (a) nature of matrix and fibre (b) nature of interphase (c) frictional damping due to slip in the unbound regions between fibre and matrix interface or delaminations and (d) damping due to energy dissipation in the area of matrix cracks and broken fibres.

The variation of tan δ with temperature at different fibre loading is given in Figure 9. The tan δ curve of PP exhibits two relaxation peaks located at 1.2693 °C (β) and at 68.4810 °C (α). The β transition corresponds to the glass transition temperature and is related to relaxation of unrestricted amorphous chains of PP. The α-transition is related to the relaxation of restricted crystalline phase of PP and can be attributed to lamellar slip mechanism and molecular chain rotation in crystalline phase. The temperature of the β_{max} is taken as the glass transition temperature. It can be seen that upon incorporation of flax nonwovens, the position of β-relaxation is not significantly altered but the presence of flax nonwovens decreased the intensity (magnitude of tan δ values) of the relaxation region. Incorporation of nonwovens acted as barriers to the mobility of polymer chains, leading to lower degrees of molecular motion and hence lowers damping characteristics. Another reason for the decrease is that there is less matrix by volume to dissipate the vibration energy[14]. The width of the tan δ peak also becomes broader than that of the pure matrix as shown in Figure 9 suggesting that there are molecular relaxations occurring at the interfacial region of the composite. It can be observed that in the α-relaxation region, the position of the peak is shifted to higher temperatures and the magnitude of tan δ values is also seen to increase. This suggests that the molecular motions in the crystalline phase are affected by the increasing flax content.

5.4.2. Effect of zein coating

5.4.2.1. Storage Modulus and tan δ

The variation of storage modulus with zein coating is given in Figure 10. It can be observed that storage modulus of the treated composites shows an increase which is more prominent in the rubbery plateau region at higher temperatures (Table 1). This can be attributed to the better reinforcing effects which increase the thermal and mechanical stability of the material at higher temperatures. Figure 11 presents the damping peaks of untreated and zein treated composites. The position of β-relaxation

was not found to be altered but in the α-relaxation region, a gradual narrowing of the peak shoulder was detected. This could be attributed to the fact that the lamellar movement in the crystalline phase being strongly affected by the zein coupling agent.

The fibre/matrix interfacial adhesion can be indirectly quantified by estimating the damping term as it is a true indicator of the molecular motions in a material. When a composite material, consisting of fibres (essentially elastic), polymeric matrix (viscoelastic), and fibre–matrix interfaces is subjected to deformation, the deformation energy is dissipated mainly in the matrix and at the interface. If matrix, fibre volume fraction and fibre orientation are identical, then the damping term can be used to assess the interfacial properties between fibre and matrix. For a weak interface, more energy is dissipated during testing and this has been reported in studies by other researchers[15]. Therefore, an interfacial strength indicator, *B*, which may be used to characterize the interfacial bonding properties, is adopted in this study to assess the potential of zein as interface modifier.

The damping property results from the inherent damping of the constituents[16] and can be represented as

$$\tan\delta_c = V_m \tan\delta_m + V_f \tan\delta_f \qquad [1]$$

As the contribution to damping from the natural fibers is negligible equation [1] reduces to

$$\tan\delta_c = \tan\delta_m \left(1 - V_f\right) \qquad [2]$$

Where tan δ is the damping value, V is the volume fraction and m, f and c represents matrix, fibre and composite respectively.

Due to significant interaction between polymer and fibre, equation [2] is rewritten as

$$\tan\delta_c = \tan\delta_m \left(1 - BV_f\right) \qquad [3]$$

Where B is a correction parameter related to effective thickness (which can be estimated from the dimensions of fibres) of the fibre-matrix interface ,which was first introduced by Ziegel and Romanov[17]. Therefore

$$B = \frac{\left(1 - \dfrac{\tan\delta_c}{\tan\delta_m}\right)}{V_f} \qquad [4]$$

Greater values of B indicate greater interfacial strength. The values of interfacial strength indicator *B* is shown in Table 2. It can be seen that interfacial strength increases with zein coating on the flax nonwovens.

5.4.3 Effect of frequency on viscoelastic properties of composites

The visco-elastic properties of a composite are dependent on temperature, time and frequency. A material that is subjected to constant stress will experience a decrease in elastic modulus over a period of time. This is due to the fact that the material undergoes molecular rearrangement in an attempt to minimize the localized stresses. The tan δ values measured over a range of frequencies (0.1, 1, 10 and 100 Hz) are shown in Figure 12. The position of β-relaxation (glass transition temperature) is found to shift to higher temperatures with increase in frequency while the magnitude decreased first and then increased at 100 Hz. The α-relaxation was found to be significantly affected with the change in frequency. The increase in frequency reduced the intensity and shifted the position of relaxation region to higher temperatures.

The relationship between the temperature at which the secondary relaxation process is observed (T) and the frequency of excitation (f) can be given by the Arrhenius equation[18].

$$f = f_0 . \exp \frac{-\Delta E_a}{RT} \qquad [5]$$

$$\log f = \log f_0 - \frac{\Delta E_a}{2.303RT} \qquad [6]$$

Where f_0 is a constant, R is the universal gas constant (8.314 $JK^{-1}mol^{-1}$) and ΔE_a is the activation energy for the relaxation. The slope of Arrhenius plot obtained by plotting log f versus 1/T will give the activation energy for that process. Table 3 presents the activation energy of the composites and it can be observed that activation energy increases, reaches to maximum at 30 % loading and then decreases. The treated composites exhibit higher activation energy than the untreated ones suggesting a higher thermal stability due to better interfacial interaction.

6. Conclusions

The effect of reinforcement of polypropylene with flax nonwovens was investigated on the basis of fibre loading. Tensile strength and modulus were found to increase with the increase in fibre loading. This was due to increase in stiffness of the composites. Flexural strength and modulus also registered an increase. Zein modification of nonwovens was found to enhance the mechanical properties of the composites. This was attributed to better interfacial bonding between matrix and nonwovens. Impact strength was found to decrease due to zein modification. Scanning electron microscopic studies revealed the presence of fibre breakage in chemically modified composites. Viscoelastic properties like storage modulus increased while damping properties were found to decrease with incorporation of flax nonwovens. Zein modification resulted in increase of storage modulus indicating better interfacial adhesion. The variation of excitation frequency was found to affect the secondary relaxations of the composites significantly. Further studies are going on to investigate the polarity changes by zeta potential measurements on flax nonwovens.

Table 1 Storage modulus and glass transition temperatures of composites (30%)

Composite	**E' at 10^{o}C [MPa]**	**E' at 60^{o}C [MPa]**	**T_g [^{o}C]**	**tan δ**
Untreated	1100 x 10^3	4900 x10^3	0.5350	0.08519
2 % Zein	1220 x 10^3	8500 x 10^3	1.6263	0.08233

Table 2 tan δ and B values of composites

Composite	**tan δ**	**V_f**	**B**
Polypropylene	0.0983	-	-
Untreated	0.08519	0.22	0.606
2 % Zein Treated	0.08233	0.20	0.812

Table 3 Activation energy of composites

Composite	**Activation energy [kJ/mol]**
Polypropylene	215.30
20 % fibre weight	257.70
30% fibre weight	410.29
40 % fibre weight	294.50
2 % Zein	482.90

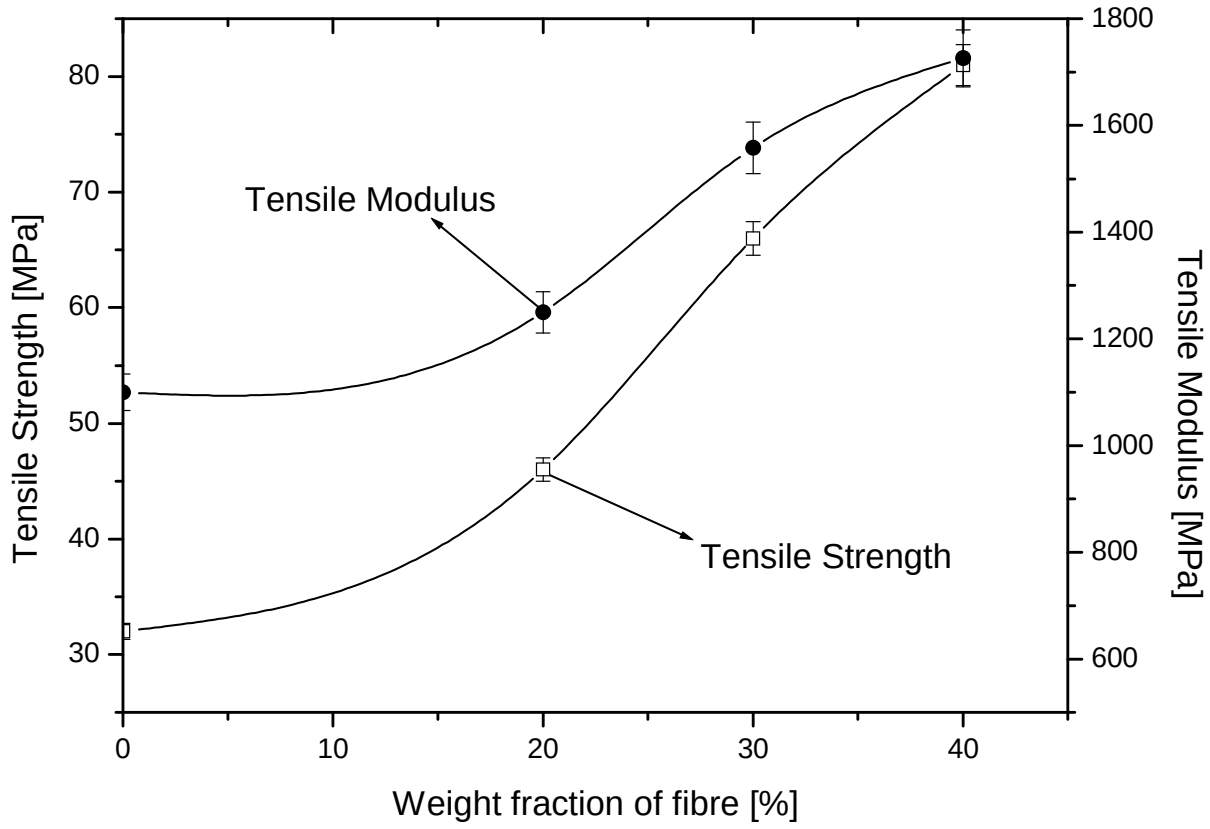


Figure 1 Effect of fibre weight fraction on tensile strength and modulus of composites

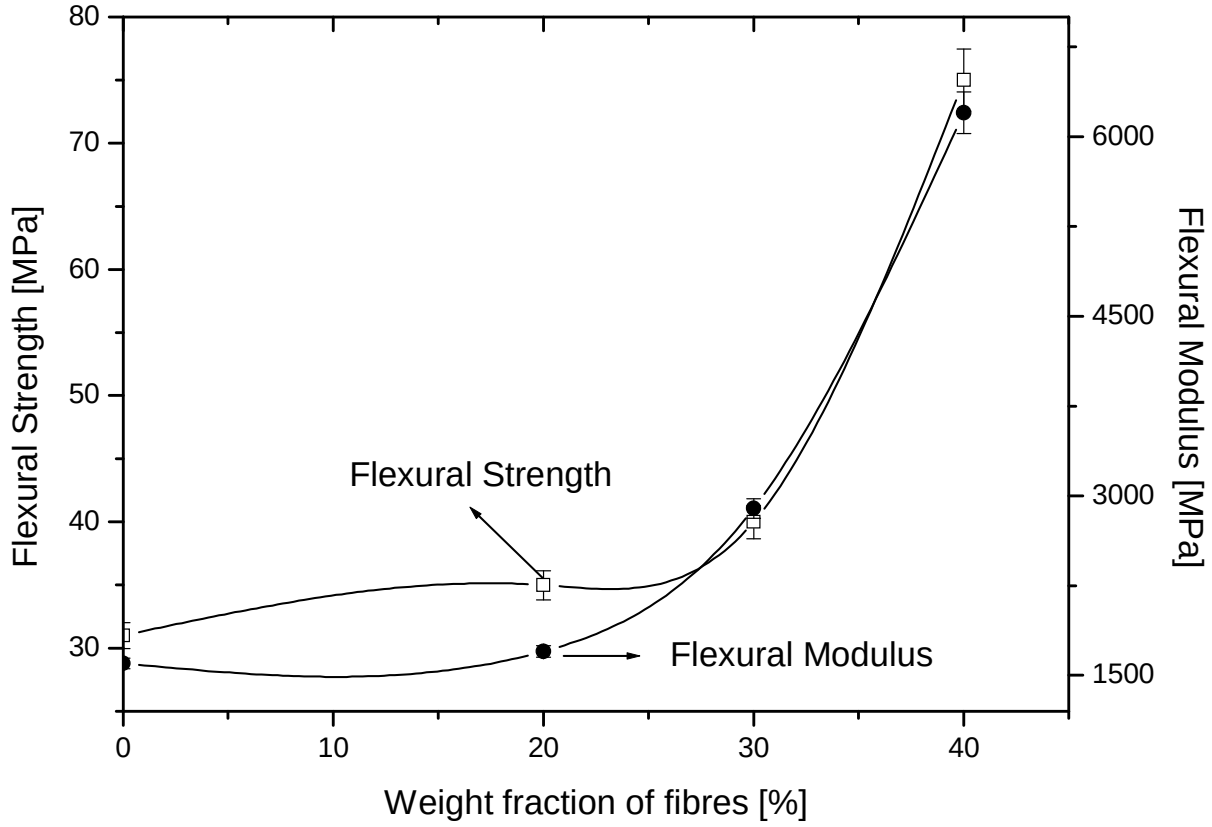


Figure 2 Effect of fibre weight fraction on tensile strength and modulus of composites

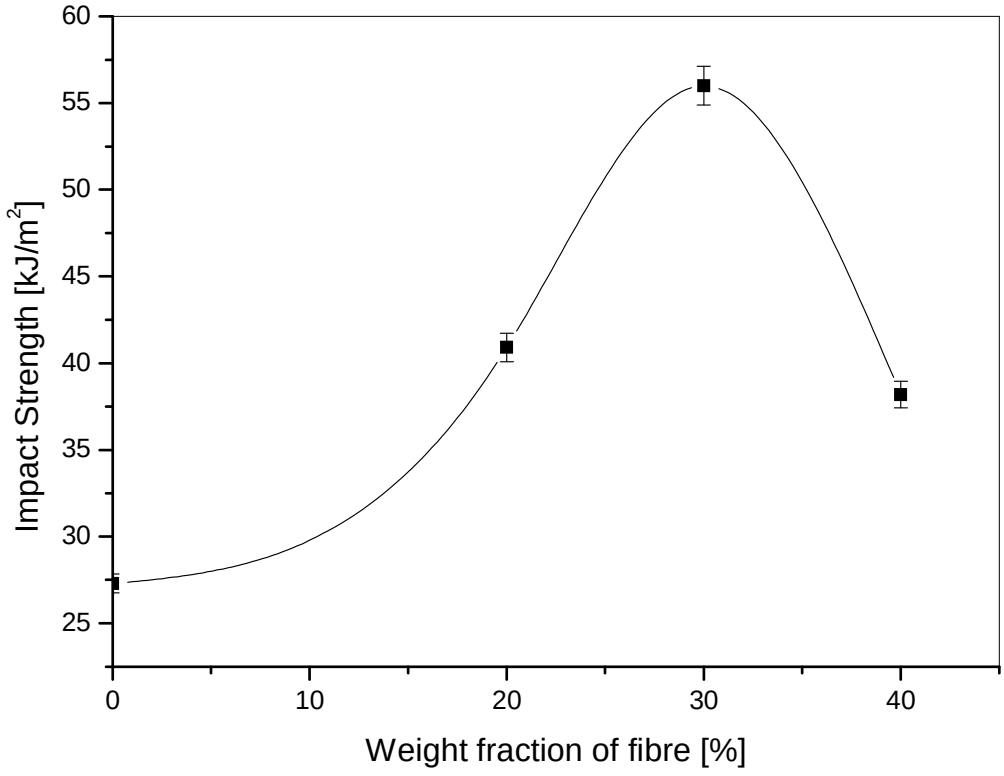


Figure 3 Effect of fibre weight fraction on impact strength of composites

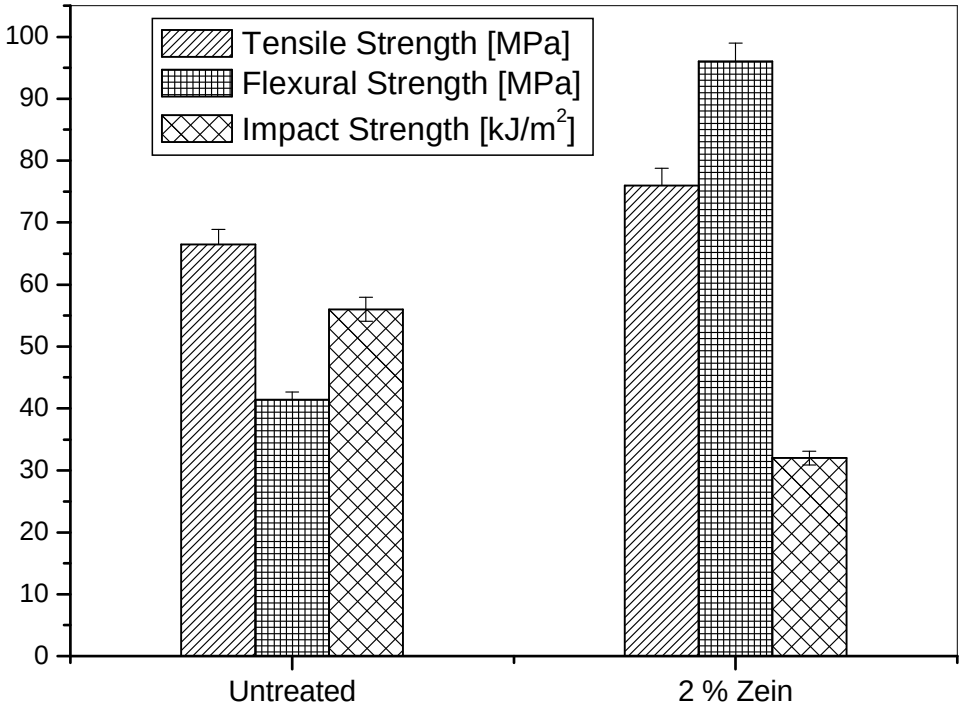


Figure 4: Effect of zein modification on mechanical properties of composite (30%).

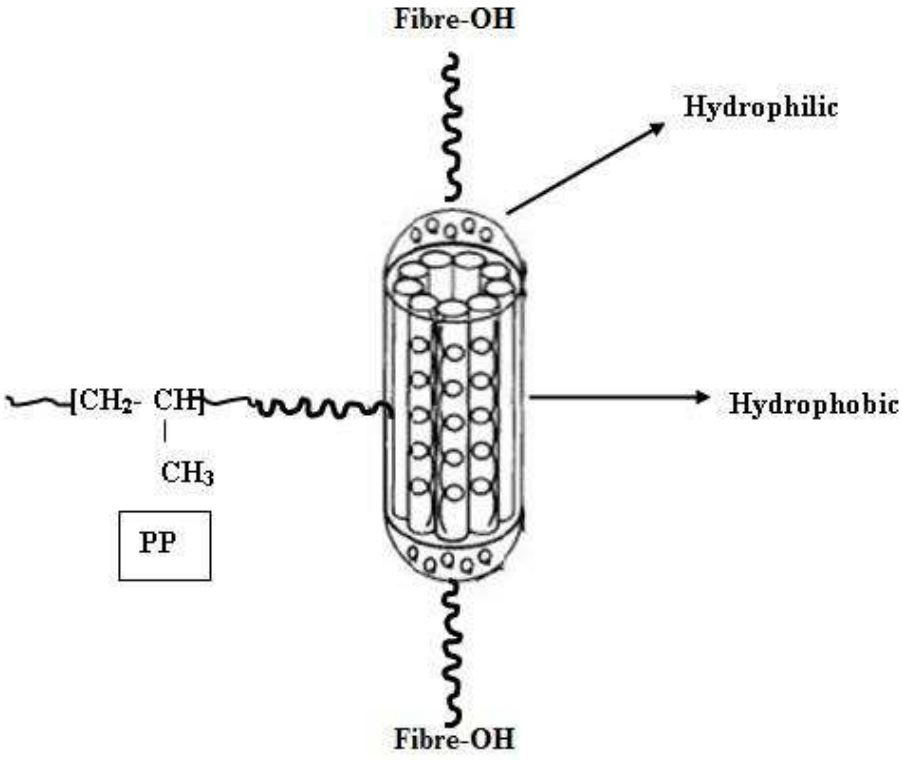
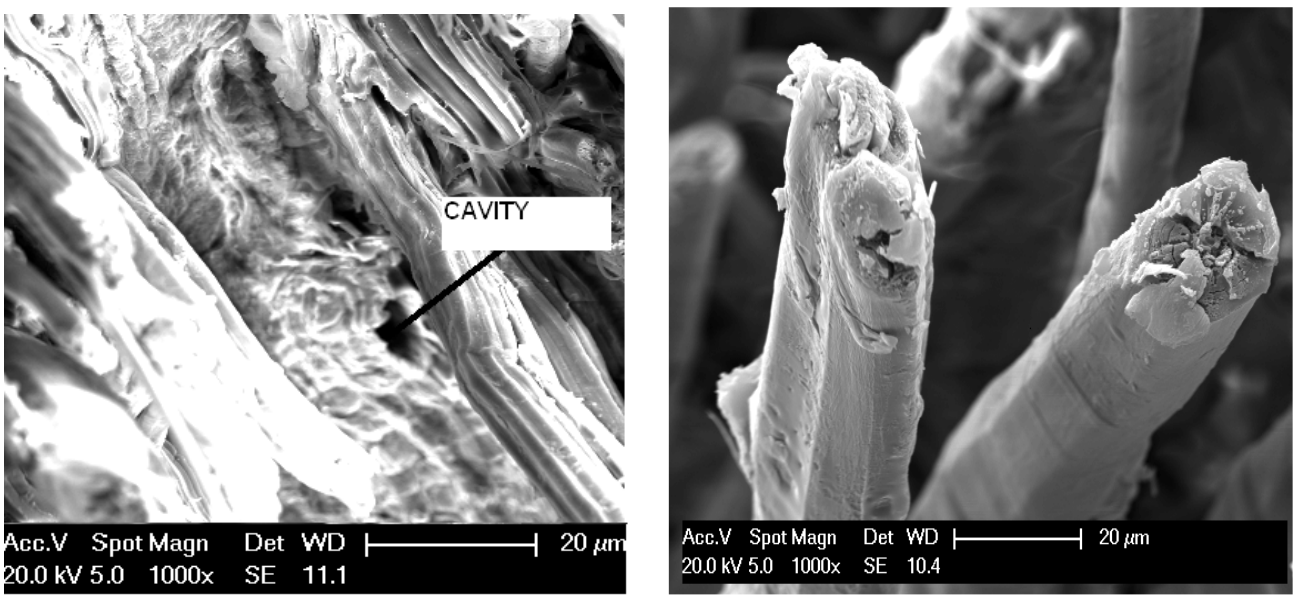


Figure 5: Schematic sketch showing the interaction between flax fibres, zein and polypropylene



(a) **(b)**

Figure 6 (a) and (b): Scanning electron micrograph of tensile fractured specimen of (a) untreated and (b) 2% zein treated composites.

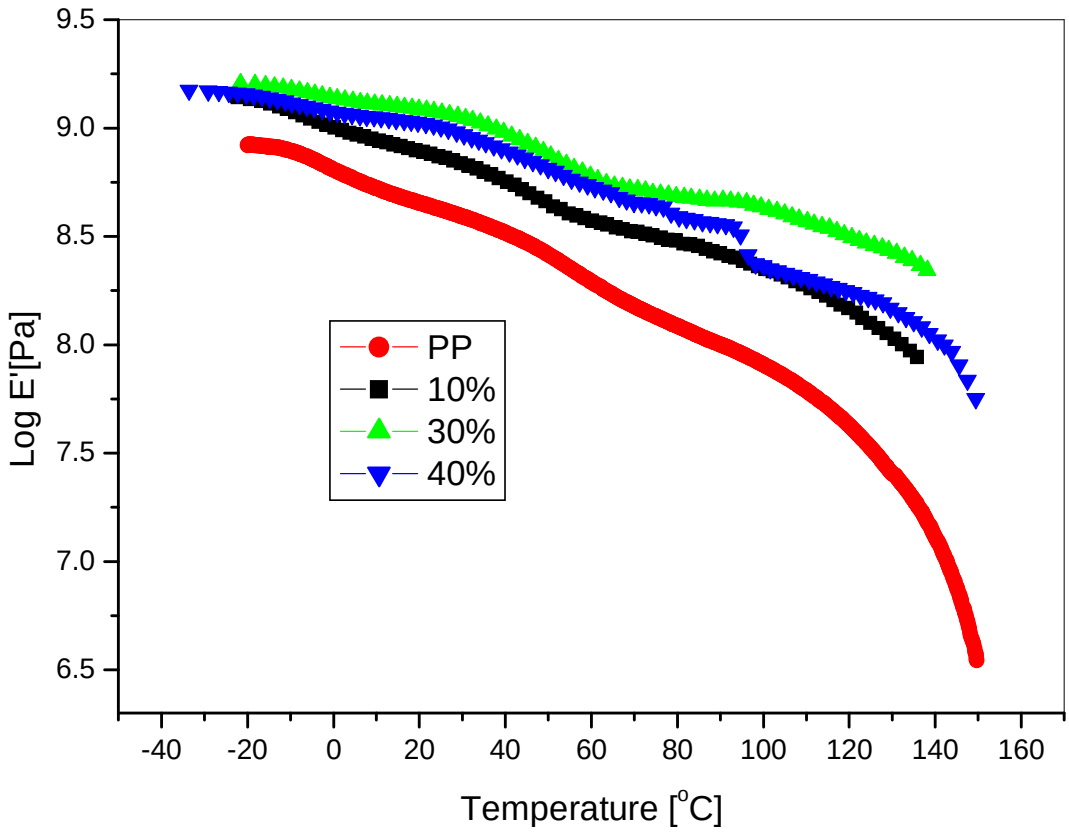


Figure 7 Storage modulus of composites at different fibre weight fractions measured at a stress amplitude of 1 Hz

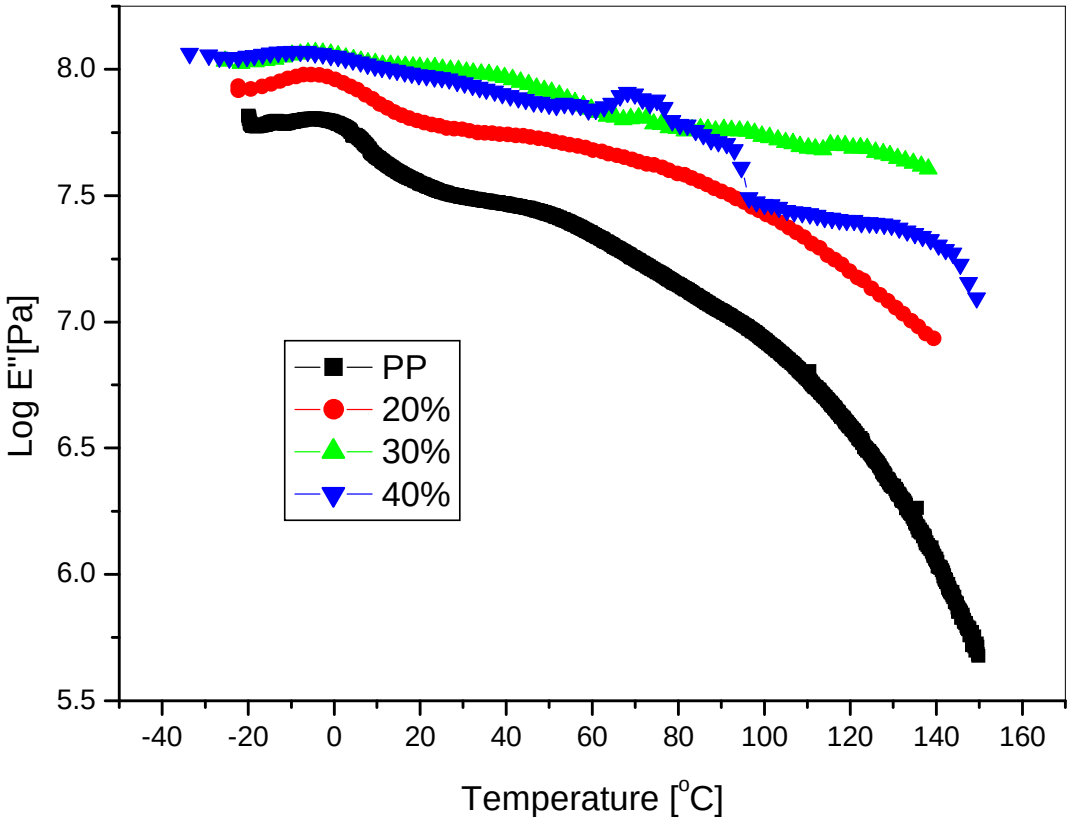


Figure 8 Loss modulus of composites at different fibre weight fractions measured at a stress amplitude of 1 Hz

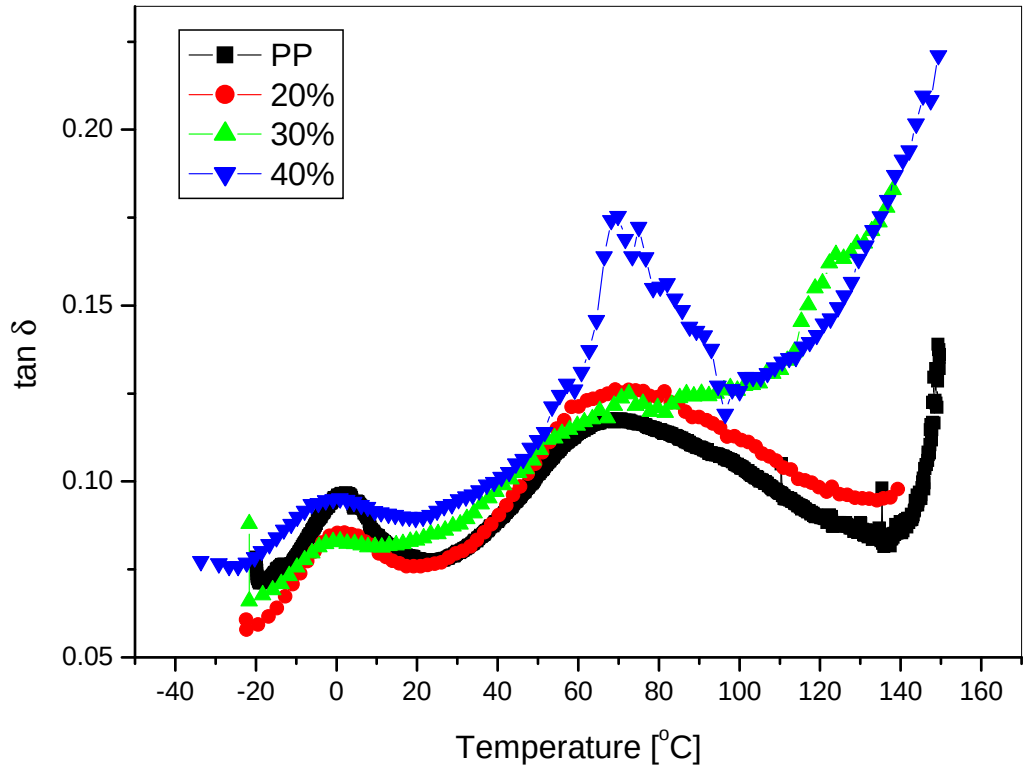


Figure 9 Variation in tan δ with temperature for composites at different fibre weight fractions at 1 Hz

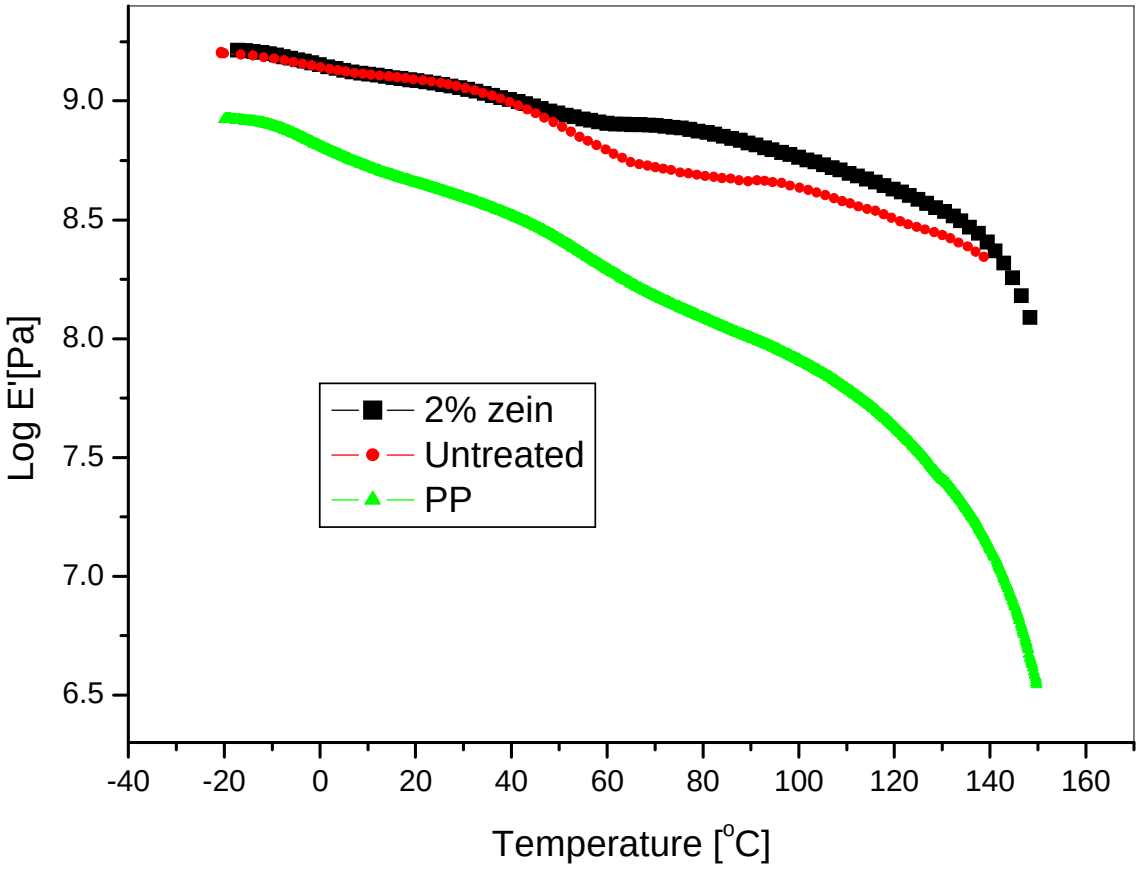


Figure 10 Variation in storage modulus for PP, untreated and zein coated composites (30%)

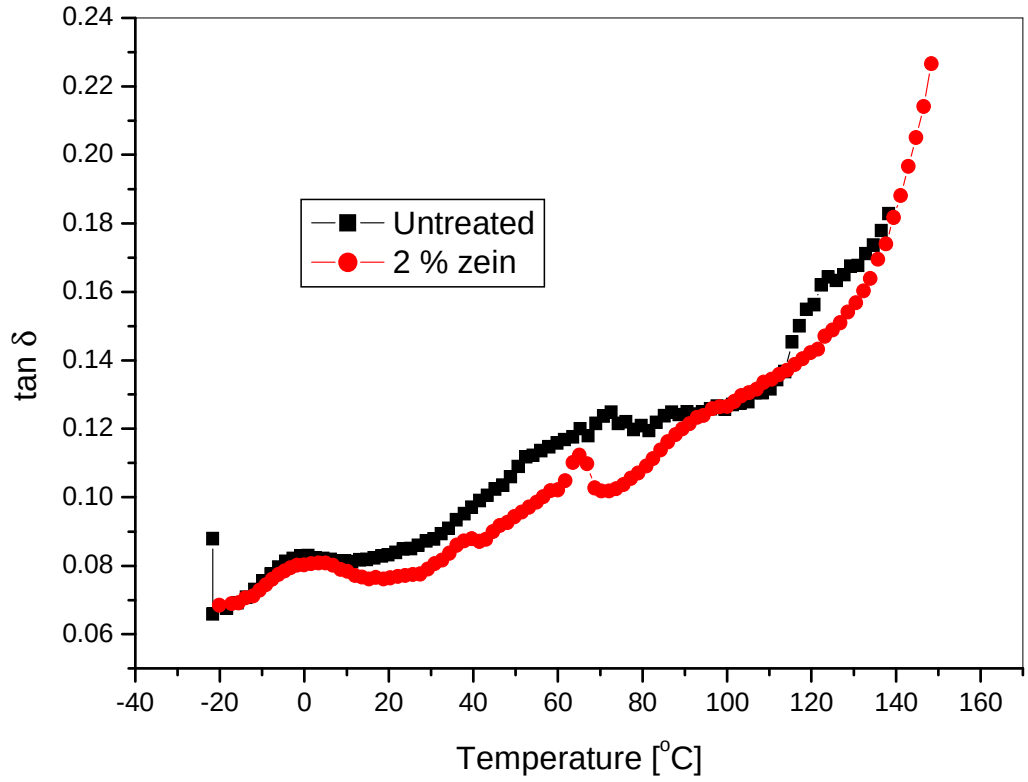


Figure 11 Variation in tan δ for untreated and zein coated composites (30%)

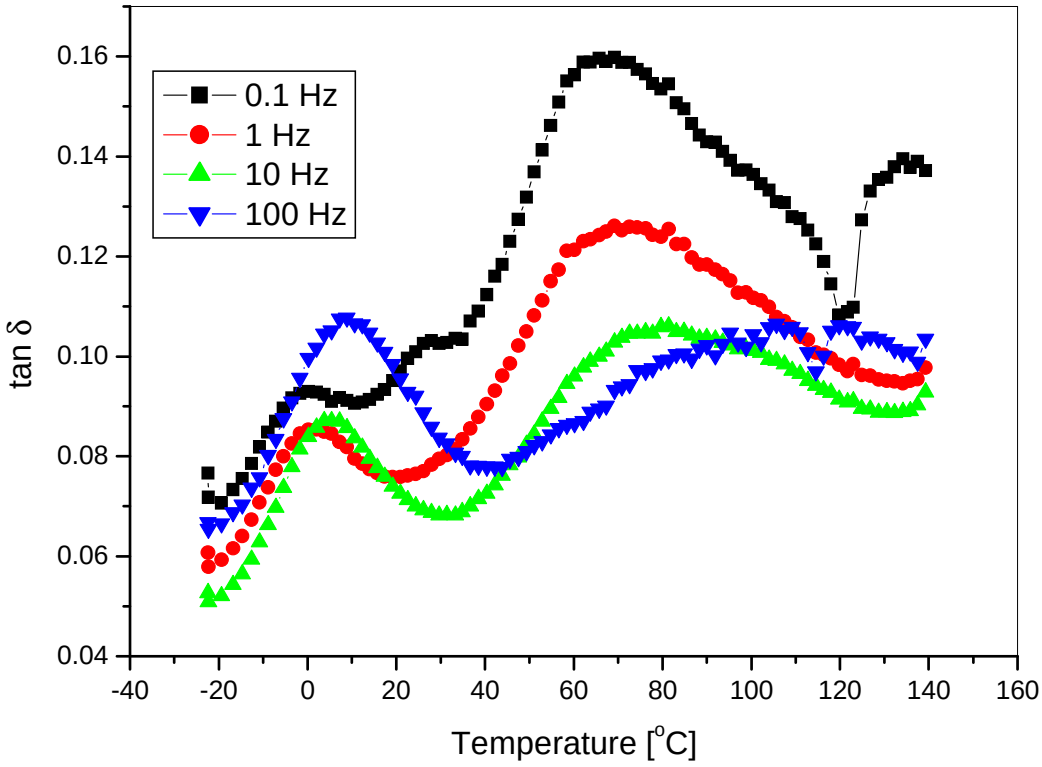


Figure 12: Variation in tan δ of composites (20%) with frequency.

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