Journal of Thermal Analysis, Vol. 47 (1996) 1121-1140

THERMOGRAVIMETRIC AND DYNAMIC MECHANICAL THERMAL ANALYSIS OF PINEAPPLE FIBRE REINFORCED POLYETHYLENE COMPOSITES

J. George, S. S. Bhagawan+ *and S. Thomas**

School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills P.O.,
Kottayam-686 560, Kerala
+Propellant Engineering Division, Vikram Sarabhai Space Centre, Thiruvananthapuram
Kerala-695 022, India

Keywords: dynamic mechanical thermal analysis, low density polyethylene, TG

Abstract

The thermal behaviour of pineapple leaf fibre (PALF) reinforced polyethylene composites was studied by thermogravimetric and dynamic mechanical thermal analysis. Fibre treatment was carried out using isocyanate, silane and peroxide to improve the interfacial adhesion between fibre and matrix. The effects of fibre loading and surface modification on the thermal properties were evaluated. It was found that at high temperature PALF degrades before the polyethylene matrix. The storage modulus increased with increase of fibre loading and decreased with increase of temperature. The treated fibre composites impart better properties compared to untreated system. Tan δ showed a distinct peak at low temperature ascribed to the glass transition temperature of polyethylene but no peak was observed for PALF fibre. The relative damping increased with fibre loading. Cole-Cole analysis was made to understand the phase behaviour of the composite samples.

Introduction

Thermal analysis is becoming an increasingly useful tool in materials characterisation. It is essential to monitor not just the final properties of the composite but also the basic raw materials through the processing cycle to the end product. Optimization of the processing temperature and time with an understanding of matrix, reinforcing element and interface between matrix and reinforcing agent, can lead to the best balance of composite properties such as modulus, thermal stability and energy damping (T_g, T_m).

Thermal properties, in particular the thermal or oxidative degradation of cellulose fibre reinforced polymer composites, have received little attention.

---

* Author to whom all correspondence should be addressed.

0368–4466/96/ $ 5.00

John Wiley & Sons, Limited
Chichester

However this is an important design factor which sets the limits of processing temperature and thereby the type of matrices that can be reinforced by these fibres. Thermogravimetric analytical (TG) technique offers a more precise control of heating condition, such as variable temperature range and accurate heating rate, and it needs only a small quantity of sample for analysis. In addition it is possible to quantify the amount of moisture and volatiles present in the composites which have a deteriorating effect. In the case of cellulose fibres, lignin degradation sets in at around 200°C, and other polysaccharides mainly cellulose are oxidized and degraded at higher temperatures [1]. Most natural fibres lose their strength at about 160°C. Thermal analysis studies of cellulose fibres have been carried out and the effects of crystallinity, orientation and crosslinking on the pyrolytic behaviour of cellulose have been reported [2–5]. Major [6] claimed that the oxidative degradation of cellulose takes place in the amorphous region. Less crystalline materials are degraded more rapidly by heat. Ramiah [7] speculated that crystallinity, crystalline size, order, degree of polymerisation and crystal structure might influence the pyrolysis rates. The effect of grafting of various polyacrylates onto cellulose and its influence on temperature and heat of degradation have been investigated by Kokta and Valde [8] using DSC and TG. Kessira and Richard [9] studied the thermal behaviour of ungrafted and methyl methacrylate and acrylate grafted Bagasse and wood pulp, loaded with $CaCO_3$.

Dynamic mechanical thermal analysis is a widely used tool for understanding structure-property relations in polymeric materials. The dynamic properties are generally expressed in terms of storage modulus, loss modulus and damping factor which are dependent on time and temperature. Much work has been done on the dynamic mechanical properties of particulate or fibrous composite materials with two objectives. First to display the chemical or physical modifications of the matrix induced by the introduction or and surface treatment of fibre and second to study the behaviour as a function of the properties of each phase. If connections exist between the phases, a shear effect is generated in the interface, which produces an increment in mechanical energy loss. When the interfacial link is lacking, the value of the energy loss is higher than that of the polymer matrix due to the fibre ends that act as stress raisers, thus contributing to mechanical energy loss [10]. Generally, the introduction of a filler in a polymeric matrix leads to reduction of the mobility of the macromolecular chains in the vicinity of filler [11–13]. This is evident from the increase in the temperature of the main relaxation, associated with the glass transition.

The aim of this work is to study the thermal properties of PALF-LDPE composites with special reference to the effect of fibre-matrix interface bonding. Untreated, peroxide, isocyanate and silane treated fibres were used for composite fabrication. The dynamic properties of these composites are examined with special reference to fibre loading and fibre treatment as a function of temperature and frequency. The effects of fibre length and fibre orientation on the dynamic mechanical properties of PALF-LDPE composites have already been reported by George *et al.* [14].

Experimental

Low density polyethylene (LDPE) [16 MA 400] was supplied by Indian Petrochemical Corporation Ltd., Vadodara. Pineapple leaf fibre (PALF) [Ananus Cosomus] was supplied by the South India Textile Research Association, Coimbatore. The physical and mechanical properties of LDPE and PALF were reported earlier [14, 15]. Fibres having a length of 6 mm and diameter of 50–150 μ were used for the experiment. Before being used they were washed with water to remove the impurities and dried in an air oven at 60°C for 24 h. Poly(methylene) poly(phenyl) isocyanate (PMPPIC) supplied by Polyscience, USA and vinyl tri-(2-ethoxy methoxy) silane [Silane A-172] supplied by Union Carbide Co., Montreal, Canada, were used as coupling agents.

Benzoyl peroxide (BPO) and dicumyl peroxide (DCP) [Reagent grade] were used as surface modifiers to improve the adhesion between fibre and matrix.

Fibre treatment

1. Silane treatment (Silane A-172)

A mixture of oven dried fibres, carbon tetrachloride, dicumyl peroxide (2% by wt. of fibre) and vinyl tri-(2-ethoxy methoxy) silane (4% by wt. of fibre) was heated under reflux for 2 h. Finally, the mixture was filtered and dried in an air oven at 60°C for 2 h.

2. Isocyanate treatment (PMPPIC)

Fibres were dipped in toluene solution containing PMPPIC (5% by wt. of fibre) for half an hour at 50°C. The fibres were then decanted and dried in an oven at 70°C for 2 h. Later these were mixed with polyethylene using toluene as the solvent containing PMPPIC (6% by wt. of fibre) at a temperature of 120°C.

3. Peroxide treatment

Benzoyl peroxide (1% by wt. of polymer) and dicumyl peroxide (0.5% by wt. of polymer) were added to the melt of polyethylene before being mixed with fibres.

Thermogravimetric analysis

Composites of PALF-LDPE were prepared by solution mixing technique as reported by George *et al.* [14, 15]. Thermogravimetric analysis (TG) and derivative thermogravimetric analysis (DTG) were carried out in a DuPont thermogravimetric analyser. Samples were scanned from 30–650°C at a heating rate of 20°C min^{-1}.

Dynamic mechanical analysis

Rectangular specimens having a size of 70×10×2 mm^3 were used for the dynamic mechanical experiments. The dynamic moduli and mechanical damping (tanδ) were measured by a direct reading dynamic viscoelastometer, Rheovibron DDV-III. The temperature range over which properties were determined was 25 to 130°C at a heating rate of 3°C min^{-1}. The samples were tested at various frequencies such as 3.5, 11 and 35 Hz. The amplitude of oscillation was 0.1%.

Results and discussion

Thermogravimetric analysis

Figure 1 shows the TG curves of LDPE, PALF and PALF-LDPE composite containing 30% fibre. Thermal decomposition of each sample takes place in a programmed temperature range of 30 to 400°C. For PALF in the temperature range 75 to 175°C dehydration as well as degradation of lignin occur and most of the cellulose is decomposed at a temperature of 350°C. The decomposition of LDPE occurs at a temperature of 400°C, which is higher than of the fibre. Fibre filled system degrades later than the polyethylene matrix as shown by

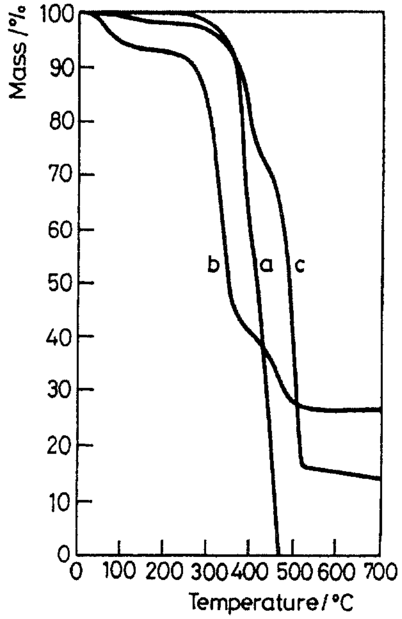


Fig. 1 TG curves of (a) LDPE, (b) PALF and (c) PALF-LDPE composite containing 20% fibre

thermogravimetric scan. It shows that thermal stability of composite is increased. Derivative thermogravimetric curves (DTG) also give evidence for this (Fig. 2).

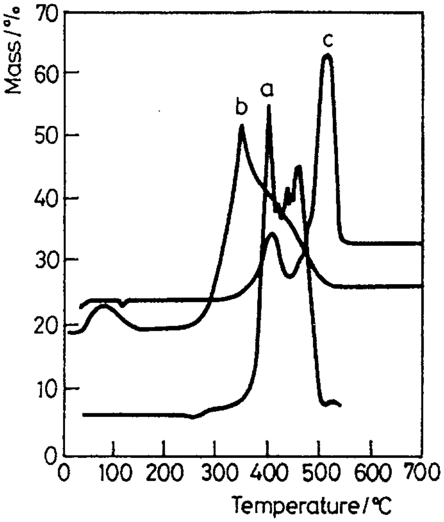


Fig. 2 DTG curves of (a) LDPE, (b) PALF and (c) PALF-LDPE composite containing 20% fibre

Step analysis of neat polyethylene thermogravimetric scan (Fig. 1) from 30–100°C shows a percentage mass drop of 0% whereas scan of PALF fibre shows a mass drop of about 6%. At 200°C the mass loss of fibre is 7.6%. This is associated with the lignin degradation. The major source of stability in cellulose is due to hydrogen bonding which allows thermal energy to be distributed over many bonds [16]. As the less ordered region increases, the decreasing mobility of cellulose chains will strain and weaken the existing hydrogen bond, thus decreasing stability. In the case of PALF about 16% weight loss occurs at 300°C while in the case of LDPE thermal decomposition starts only at 250°C. In PALF-LDPE composites a slight degradation occurs at 150°C due to the dehydration and the main decomposition is shifted to higher temperature region. Thus on comparing the weight losses at 300°C, it can be seen that the values are 16, 2 and 3.2% for PALF, LDPE and PALF-LDPE composites, respectively. Weight losses at different temperatures are shown in Table 1. At temperature of 550°C, PE is completely decomposed. But in PALF and fibre composites a residue of 94 and 84.8% , respectively was observed. This may be of carbonaceous products. Kilzer and Broido [17] reported that thermal pyrolysis of whole cellulosic material occurred through two simultaneous and competitive mechanism, dehydration at about 200 to 270°C involving mainly loss of water to yield a dehydrocellulose and stepwise depolymerisation to yield a levo glucose above 270°C. Formation of latter is characteristic of crystalline region.

Table 1. Weight losses at different temperatures

Material	Weight loss/%			
	100°C	200°C	400°C	450°C
PALF	6	16.0	58.8	62.8
LDPE	0	2.0	40.0	86.0
PL_U[a]	1	3.2	18.8	30.0
PL_P[b]	1	3.2	16.0	24.0
PL_B[c]	1.2	3.2	24.0	30.8

PL – PALF-LDPE composite
a – Untreated fibre composite
b – PMPPIC treated
c – BPO treated

In DTG curve, a peak is observed at 75°C in PALF which corresponds to the dehydration (Fig. 2). The major peak at 350°C corresponds to the thermal degradation of dehydrocellulose. The DTG curve of LDPE shows a peak at 400°C which indicates the degradation of saturated and unsaturated carbon atoms in polyethylene. In PALF-LDPE composite two peaks were obtained. The minor peak at 410°C corresponds to degradation peak of PE and the major peak at 510°C corresponds to the degradation of dehydrocellulose. It is interesting to note that in the composite the major peak is shifted to higher temperature region

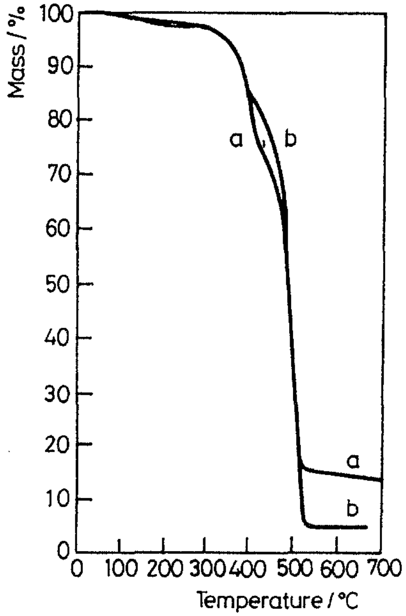


Fig. 3 TG curves of PALF-LDPE composites: Effect of different fibre treatments. (a) Untreated fibre, Fibre content 20%, (b) PMPPIC treated, 20%

compared to PALF and LDPE peak, i.e., thermal stability is increased in composite compared to pure PALF due to improved fibre-matrix interaction. This can be further understood from the weight losses at a definite temperature, for example, the weight losses at 400°C for PE, PALF and PALF-LDPE composites are 40, 58.8 and 18.8%, respectively.

The extent of degradation of PALF-LDPE composite treated with PMPPIC is less at a given temperature than of the untreated fibre composite which is evident from Figs 3 and 4. When comparing the weight losses at 450°C they are 30% for the untreated composite containing 20% fibre and 24 and 30.8% for PMPPIC and BPO treated composite, respectively. The slightly higher thermal stability of treated fibre composite can be explained by the additional intermolecular bonding between fibre and matrix induced due to isocyanate and peroxide treatment. The PMPPIC treatment of the fibre makes the composites thermally more stable than the untreated one. This is associated with the better interaction between fibre and matrix, due to the formation of covalent bond between the –N=C=O group of PMPPIC and –OH group of cellulose.

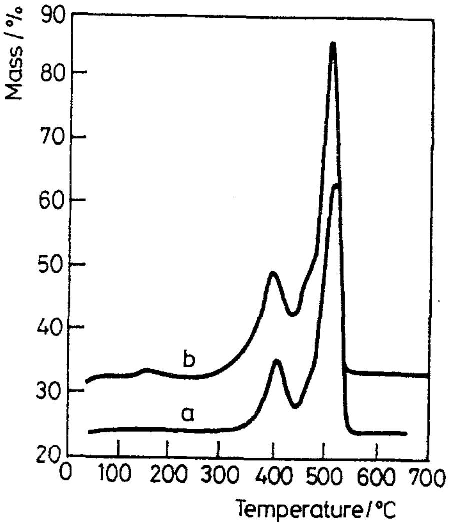


Fig. 4 DTG curves of PALF-LDPE composites: Effect of different fibre treatments. (a) Untreated fibre, Fibre content 20%, (b) PMPPIC treated, 20%

Dynamic mechanical thermal analysis

Dynamic moduli of composites depend on matrix type and fibre loading. Figure 5 shows the temperature dependence of storage modulus E' and tanδ for LDPE and composite filled with 10% PALF fibre. Fillers have a large effect in increasing the modulus of polymeric materials. Addition of fibres increases thus the modulus. At low temperature, E' values of PE and composite are very close,

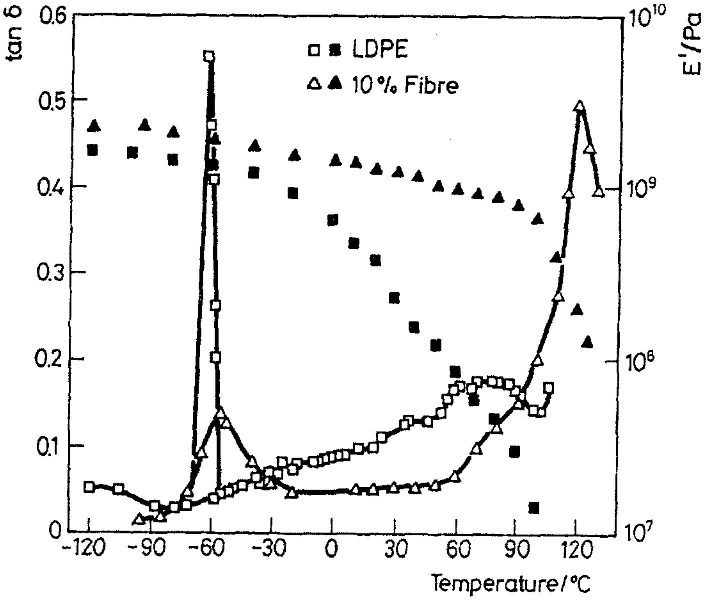


Fig. 5 Storage modulus (*E'*) and tanδ as a function of temperature

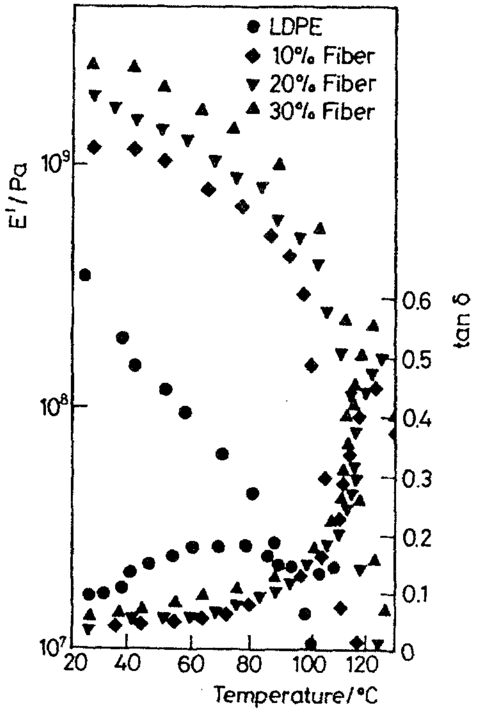


Fig. 6 Effect of fibre loading on *E'* and tanδ of PALF-LDPE composites. Oscillation frequency 35 Hz

i.e., 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. In pure PE, E' drops steeply on increasing the temperature due to the increased segmental mobility. In the case of tan δ as seen in Fig. 5, two peaks were obtained one at low temperature and other at higher temperature. The relaxation spectra of composites in the transition regions depend mainly on the mechanical relaxation of matrix and loaded fibre and are affected to different extent by the interface between fibre and matrix. Normally, tanδ values of polymer composites show two dispersion peaks one at low temperature corresponding to the main relaxation of the matrix and another at high temperature due to the relaxation of the loaded fibres. In the case of neat PE, the peak at a temperature of –65°C is due to the glass transition of PE. The high temperature peak at 78°C is associated with the onset of melting of the PE crystallites. In the case of fibre filled system, it is interesting to note that the T_g and T_m are shifted to higher temperature, i.e., –65 to –55°C and +70 to

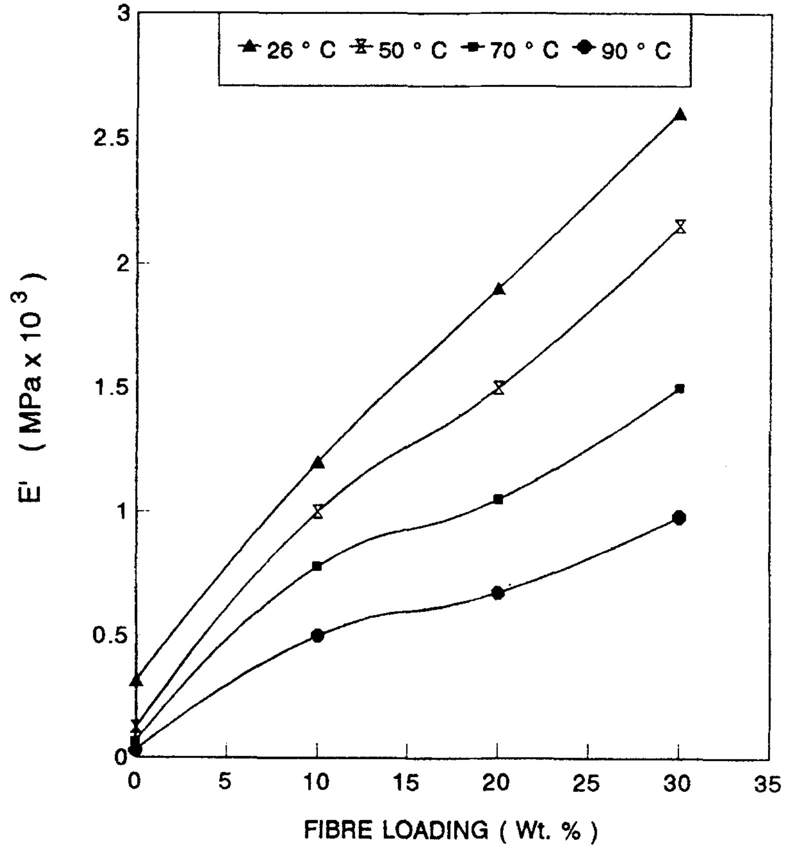


Fig. 7 Effect of fibre loading on E' and tanδ of PALF-LDPE composites at different temperatures

+120°C, respectively. This is associated with the decreased mobility of the chains by the addition of fibres. The damping peak of the composites is lower and broader than that of polyethylene. This is due to the fact that, when strain is applied to the fibres, the greater stiffness of the fibres causes the strain to be controlled by the fibres in such a way that the interface which is assumed to be the more dissipative component of the composite is strained to a lesser degree [18, 19].

Effects of fibre loading on *E′* with untreated PALF have already been reported [14]. Figure 6 shows the effect of fibre loading on storage modulus and tanδ of silane treated PALF-LDPE composites. *E′* depends largely on fibre loading and increases with fibre loading. At any particular temperature the storage modulus increases with fibre loading and decreases with increasing temperature which is clearly evident from Fig. 7. The increase in modulus with fibre loading indicates that LDPE matrix gets stiffened by the addition of fibres. All the filled system display similar dependence of *E′* with temperature (Fig. 6). The decrease of *E′* with temperature is gradual up to 90°C. At 90° all the filled system exhibit nearly the same modulus and the influence of fibre in stiffening the matrix is marginal due to the melting of polyethylene crystallites. Compared to PE, *E′* of composite becomes flatter and extends to the higher temperature side with fibre loading indicating the increased thermal stability of the compos-

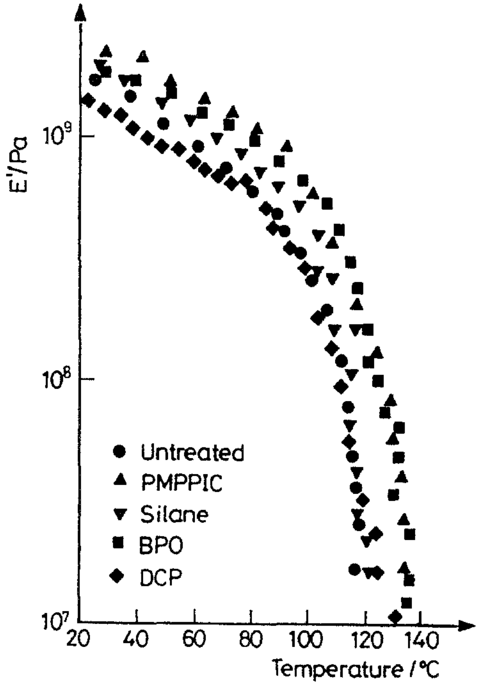


Fig. 8 Effect of different chemical treatment on *E′* of PALF-LDPE composites

ites. From the Fig. 6 it is clear that, tanδ values increase with temperature. The peak observed at 78°C in LDPE corresponds to the melting of PE crystallites. The maximum value of relaxation peak (melting) increases with increase of fibre loading.

Effect of coupling agent

Fibre surface treatment has great influence on the dynamic mechanical properties of composites. The effects of chemical treatments on the *E′* of PALF-LDPE composites at 20% fibre loading at the frequency of 35 Hz is shown in Fig. 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 achieved through more intense fibre-matrix interaction. This improvement increases with the fibre loading which is evident from Fig. 9. Introduction of functional groups by the coupling agents enhances

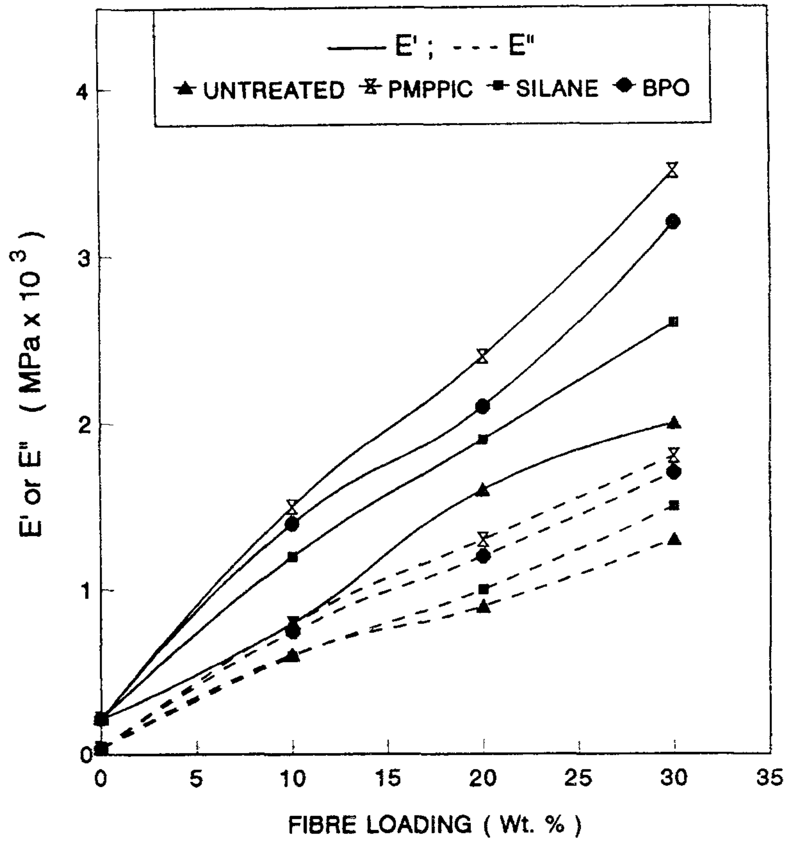


Fig. 9 Effect of chemical treatments on *E′* and *E″* of PALF-LDPE composites at different fibre loading. Temperature 26°C

the fibre-matrix adhesion resulting in lesser molecular mobility in the interfacial region. The maximum improvement is observed in the case of PMPPIC treated composite. The improved performance of PMPPIC treated fibres is attributed to the formation of covalent bonds between the –OH group of cellulose and the –N=C=O group of PMPPIC. The isocyanate groups readily react with cellulose and lignin hydroxyls to form urethane linkages. In the case of PMPPIC treated composite a peak is observed at 35°C which may be due to interface effect. Increase in modulus observed in silane treated fibre is due to the formation of hydrogen bond between silanol and –OH group of cellulose [20, 21]. The possible hypothetical structure in the interfacial area is shown in Fig. 10. The general formula for the silane coupling agent is $YR_1\,Si(OR_2)_3$. The $-OR_2$ unit is susceptible to water and during coating it may hydrolyse to some extent to form silanols.

$$YR_1\,Si(OR_2)_3 \xrightarrow{H_2O} YR_1\,Si(OH)_3 \qquad (1)$$

In this *Y* is the polymerisable vinyl group of silane. Dicumyl peroxide which is used as an initiator during coating treatment helps to polymerize vinyl groups. Individual silane coupling agent molecules which are supposed to attach to cellulose forms thus a continuous chain. The long hydrophobic polymer chain of polymerized silane can adhere to PE due to Van der Waal's type adhesive force. As a result, silane coupling agents form a bridge at the interface.

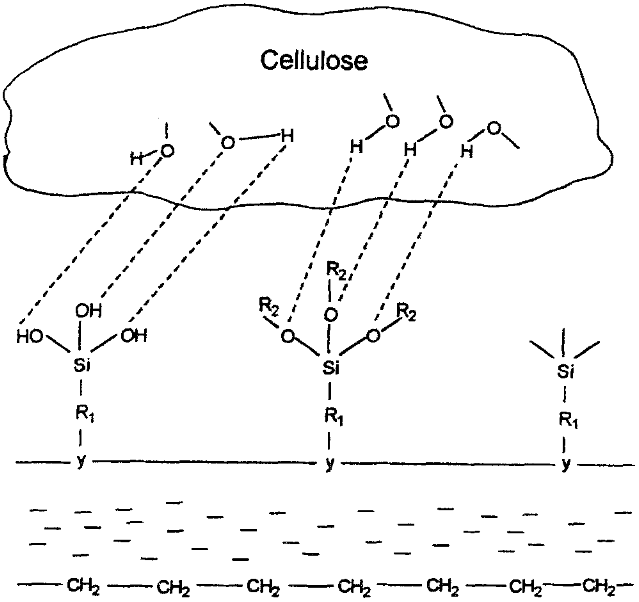


Fig. 10 Schematic representation of cellulose-silane-LDPE composites of the interfacial area

It is clear from the figure that peroxide treated systems exhibit higher modulus than the untreated fibre, at the same loading. This increase in modulus in peroxide modified composites is related to peroxide-initiated free radical reactions between LDPE and cellulose fibres [22, 23].

$$RO - OR \rightarrow 2RO^{\cdot} \tag{2}$$

$$RO^{\cdot} + PE - H \rightarrow ROH + PE^{\cdot} \tag{3}$$

$$RO + \text{Cellulose} - H \rightarrow ROH + \text{Cellulose}^{\cdot} \tag{4}$$

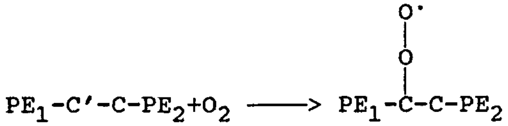
The hydrogen abstraction in cellulose occurs from –OH, C–H of the cellulose backbone as well as from methylol (–CH_2–OH) groups.

During processing the following reaction may take place.

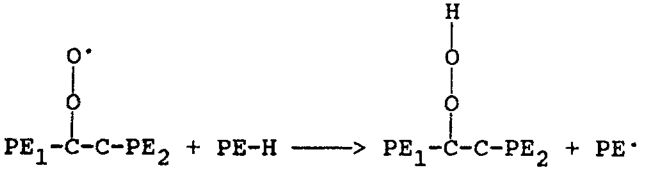
1. Increase of molecular weight and crosslinking of polymer-matrix by recombination of the macroradicals of polyethylene.

$$PE^{\cdot} + PE^{\cdot} \rightarrow PE - PE \tag{5}$$

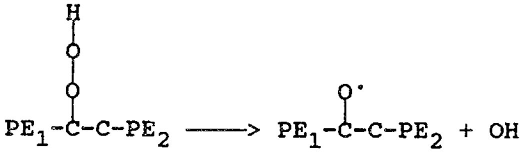
2. Introduction of polar groups (such as acidic and ketonic) into the nonpolar polyethylene chains by oxidative degradation.



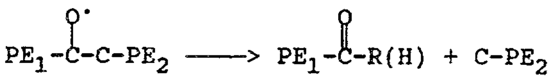
$$PE_1\text{-}C'\text{-}C\text{-}PE_2 + O_2 \longrightarrow PE_1\text{-}\overset{\substack{O^{\bullet}\\|\\O\\|}}{C}\text{-}C\text{-}PE_2 \tag{6}$$



$$PE_1\text{-}\overset{\substack{O^{\bullet}\\|\\O\\|}}{C}\text{-}C\text{-}PE_2 + PE\text{-}H \longrightarrow PE_1\text{-}\overset{\substack{H\\|\\O\\|\\O\\|}}{C}\text{-}C\text{-}PE_2 + PE^{\bullet} \tag{7}$$



$$PE_1\text{-}\overset{\substack{H\\|\\O\\|\\O\\|}}{C}\text{-}C\text{-}PE_2 \longrightarrow PE_1\text{-}\overset{\substack{O^{\bullet}\\|}}{C}\text{-}C\text{-}PE_2 + OH \tag{8}$$



$$PE_1\text{-}\overset{\substack{O^{\bullet}\\|}}{C}\text{-}C\text{-}PE_2 \longrightarrow PE_1\text{-}\overset{\substack{O\\\|}}{C}\text{-}R(H) + C\text{-}PE_2 \tag{9}$$

3. Grafting of polyethylene onto cellulose fibres by recombination of cellulose and polyethylene radicals.

$$PE^{\bullet} + Cellulose^{\bullet} \rightarrow PE - Cellulose \tag{10}$$

DCP does not have any effect on increasing the *E′* of composite. This may result from the relative rates of peroxide decomposition, i.e., decomposition temperature of DCP is 140°C. But in PALF-LDPE composite the mixing was carried out at 120°C. At this temperature DCP does not have any influence on imparting a better interaction between fibre and matrix.

The effect of surface treatment on the tanδ of the composite is shown in Fig. 11. In the case of PMPPIC treated composite a peak is observed at 35°C which correspond to the interface effect. A similar trend is observed in the modulus too as evident from Fig. 9. This increase in modulus is associated with the better interaction between fibre and matrix due to isocyanate treatment. The

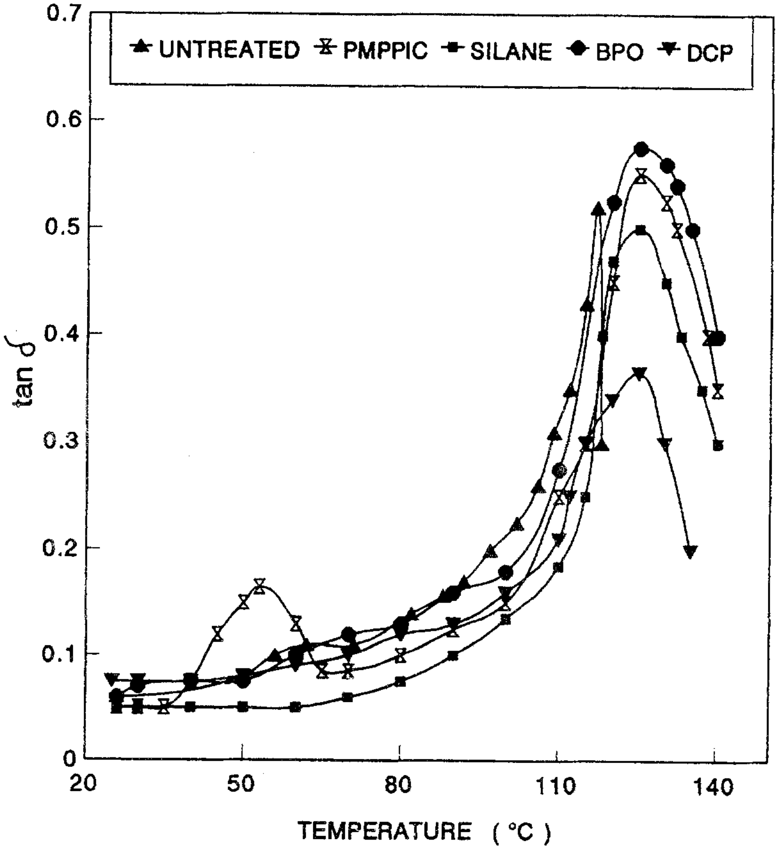


Fig. 11 Effect of chemical treatments on tanδ of PALF-LDPE composites at different temperatures

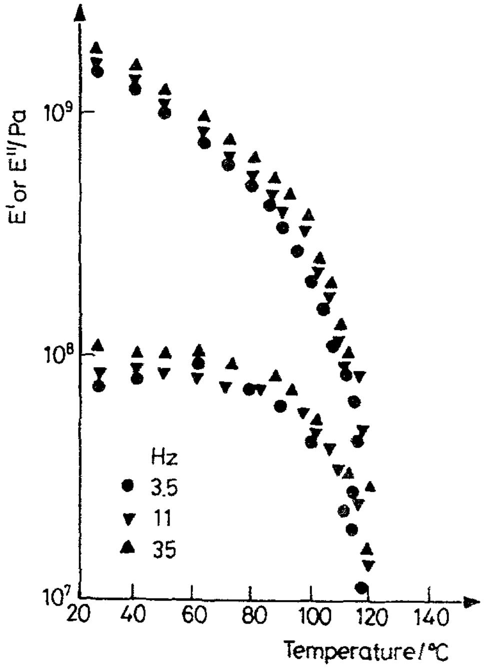


Fig. 12 Effect of oscillation frequency on E' and E'' of untreated composites. Fibre loading 20%

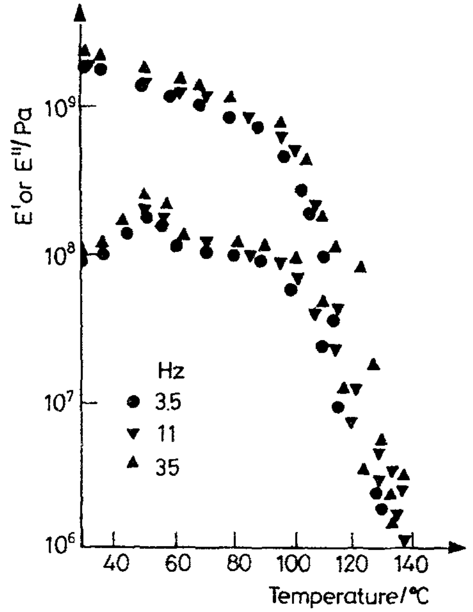


Fig. 13 Effect of oscillation frequency on E' and E'' of PMPPIC treated composites. Fibre loading 20%

melting peak is shifted to the higher temperature region in treated composites. The damping of composite increases proportionately to the increase of the modulus.

Effect of frequency

The viscoelastic properties of a material are dependent on temperature and time (frequency). If a material is subjected to a constant stress its elastic modulus will decrease over a period of time. This is due to the fact that the material undergoes molecular rearrangement in an attempt to minimise the localized stresses. Modulus measurements performed over a short time (high frequency) result thus in higher values whereas measurements taken over long times (low frequency) result in lower values.

On varying the oscillation frequency, changes occur in both *E′* and *E″* of untreated and PMPPIC treated composites as evident from Figs 12 and 13. The value of *E′* tends to increase with frequency at a given temperature. This is attributed to the lesser mobility of polymeric chains at higher frequency.

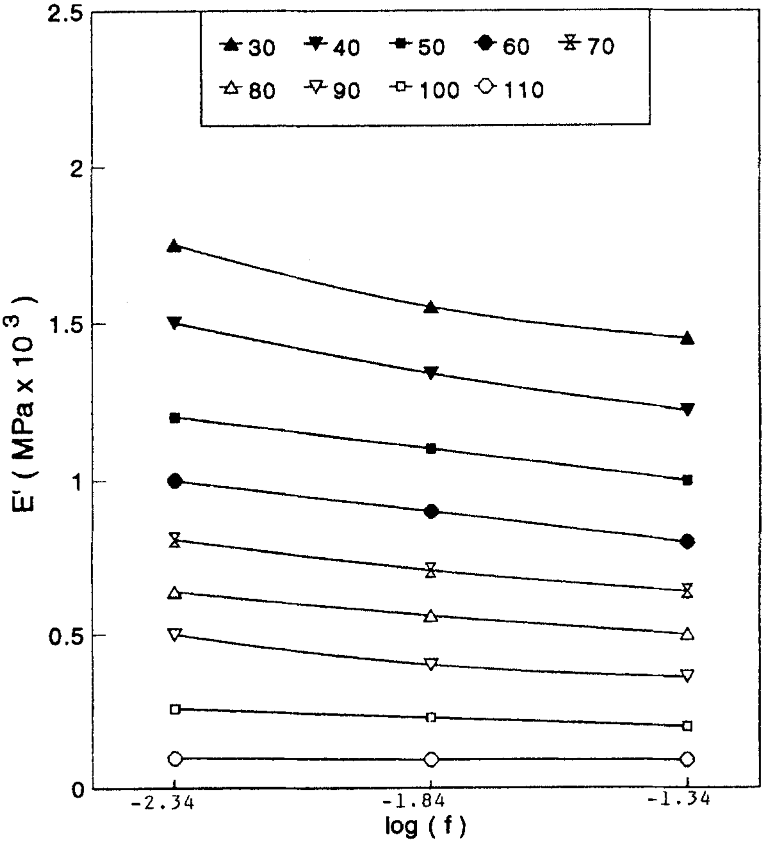


Fig. 14 *E′* *vs.* log*f* curves of PALF-LDPE composites for temperatures from +30 to 110°C

The viscoelastic properties at a given frequency 'f' is quantitatively equivalent to those of an experiment carried out over a time $t=1/2\pi f$. Viscoelastic data collected at one given temperature can be superimposed upon data collected at different temperatures by shifting the curves, i.e., by using the time-temperature superposition principle [24, 25]. Figure 14 shows the E' *vs.* log frequency graph for temperatures from +30°C to 110°C. Here experimental curves of the modulus for different temperatures are plotted against log$f$. The modulus curve at a particular temperature is then shifted along the frequency axis until overlaps with the next curve. The distance between curves give the value of the shift factor loga_T. The shift factor a_T characterizes the rate of the relaxation mechanism at some temperature T_i in comparison with the rate at a higher temperature T_{i+1}. In this way loga_T values for all temperatures were determined. The temperature of 110°C was taken as the reference temperature in constructing the loga_T *vs.* T graph illustrated in Fig. 15. On this curve the value for a given temperature T shows how many times slower the relaxation mechanism at that particular temperature takes place than at the reference temperature, $T_m=110$°C of

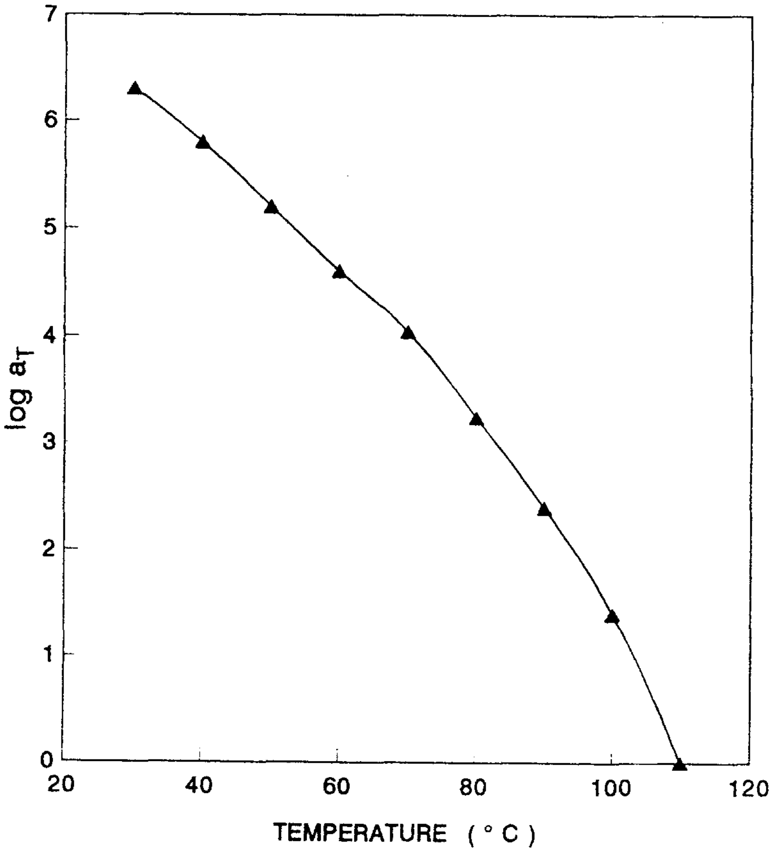


Fig. 15 Plot of loga_T *vs.* T

the range under study. Using the time temperature superposition principle it is possible to predict the viscoelastic behaviour of a material well outside of the frequency or time range of mechanical equipment.

Figure 16 shows the Cole-Cole plot, where the loss modulus (*E*″) data are plotted as a function of the storage modulus (*E*′). It is reported that homogeneous polymeric systems show a semicircle diagram whilst two-phase systems show two modified semicircles [19, 26]. In the present case the composites show a behaviour different from homogeneous system, possibly because of the presence of dispersed fibres and of the different interphase effects.

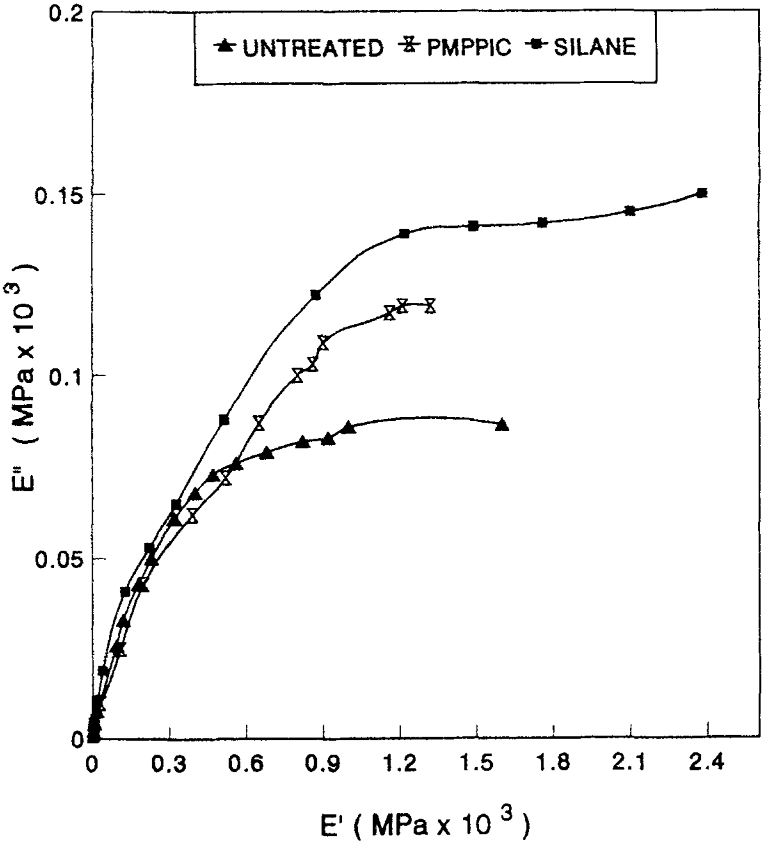


Fig. 16 Cole-Cole plots of PALF-LDPE composites

Conclusion

Thermogravimetric properties of PALF-LDPE composites have been studied with special reference to fibre loading and fibre treatment. It was found that PALF degraded before the polyethylene matrix. In the case of PALF at a temperature range of 30–180°C lignin is degraded and at 350°C most of the cellulose is decomposed. The decomposition of LDPE takes place at a temperature of 400°C. In PALF-LDPE composite, two peaks were obtained. A minor peak at 410°C corresponds to the degradation peak of PE and the major peak at 510°C corresponds to the degradation of dehydrocellulose, i.e., thermal stability is increased in composites due to better fibre-matrix interaction. Dynamic properties of composites were studied as a function of temperature and frequency. The different parameters investigated were again fibre loading and fibre-treatment. E' was found to be increased with fibre loading. At a temperature of 90°C the differences in moduli were marginal due to the melting of polyethylene matrix. The $\tan\delta$ curve at low temperature side showed a peak at –65°C corresponding to glass transition temperature of polyethylene. By the addition of 10% fibre this peak was shifted to higher temperatures and damping was reduced.

Different chemical treatments were done to improve the adhesion between fibre and matrix and interface properties have been studied by DMA by increasing the temperature and frequency. It was found that the improved interaction exerted by the chemical treatments makes the composite more mechanically and thermally stable than the untreated fibre composite. Dynamic moduli increased with increasing frequency due to the reduced segmental mobility. Time–temperature superposition curve is generated by shifting the curve at a particular temperature to the reference temperature in order to gain an insight into the viscoelastic behaviour of the material outside the used frequency range. Finally, the Cole-Cole of the composite indicated the heterogeneous nature of the system.

* * *

One of the authors (J. George) is thankful to Council of Scientific and Industrial Research, New Delhi, for financial support.

References

1 K. Akita and M. J. Kase, Polym. Sci. A-1, 5 (1967) 833.
2 A. Basch and M. Lewin, J. Polym. Sci., Polym. Chem. Ed., 11 (1973) 3071.
3 A. Basch and M. Lewin, J. Polym. Sci., Polym. Chem. Ed., 11 (1973) 3097.
4 A. Basch and M. Lewin, J. Polym. Sci., Polym. Chem. Ed., 12 (1974) 2053.
5 H. Rodrig, A. Basch and M. Lewin, J. Polym. Sci., Polym. Chem. Ed., 13 (1975) 1921.
6 W. D. Major, Tappi, 41 (1956) 530.
7 M. V. Ramiah, J. Appl. Polym. Sci., 14 (1970) 1323.
8 B. V. Kokta and J. L. Valde, Tappi, 55 (1972) 375.
9 L. Kessira and A. Richard, J. Appl. Polym. Sci., 49 (1993) 1603.
10 V. M. Murty, S. K. De, S. S. Bhagawan, R. S. Krishna and S. K. Athithan, J. Appl. Polym. Sci., 28 (1983) 3845.
11 D. H. Droste and A. T. Di Benedetto, J. Appl. Polym. Sci., 13 (1969) 2149.
12 G. J. Howard and R. A. Shanks, J. Macromol. Sci. Phys., B19 (1981) 167.
13 M. V. Boluk and P. H. Schreiber, Polym. Compos., 7 (1986) 295.

14 J. George, K. Joseph, S. S. Bhagawan and S. Thomas, Mater. Lett., 18 (1993) 163.
15 J. George, N. Prabhakaran, S. S. Bhagawan and S. Thomas, J. Appl. Polym. Sci., 57 (1995) 843.
16 N. J. Chu, J. Appl. Polym. Sci., 14 (1970) 3129.
17 F. J. Kilzer and A. Broido, WSS/C1 Paper 64-4, Stanford University, 1964.
18 W. Guo and M. Ashida, J. Appl. Polym. Sci., 56 (1993) 1435.
19 L. Ibarra, M. Macias and E. Palma, J. Appl. Polym. Sci., 57 (1995) 831.
20 D. Maldas, B. V. Kokta and C. Daneault, J. Appl. Polym. Sci., 37 (1989) 751.
21 F. D. Ozterholz, Moden Plastics Ency., 63 (10A) (1986-1987) 126.
22 B. N. Misra, I. K. Mehta and R. C. Khetarpal, J. Polym. Sci. Polym. Chem. Ed., 22 (1984) 230.
23 S. Sapieha, P. Allard and Y. H. Zang, J. Appl. Polym. Sci., 41 (1990) 2039.
24 J. D. Ferry, 3rd Edn., Wiley, New York, 1980.
25 M. L. William, R. F. Landel and J. D. Ferry, J. Am. Chem. Soc., 77 (1954) 3701.
26 C. Wismie, G. Maria and P. Monge, Eur. Polym. J., 21 (1985) 479.