

The Influence of Dimethyl Hydrogen Siloxane on Polypropylene-Straw Fibres Interface

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ABSTRACT

This paper describes the characteristics of polypropylene-straw fibres composite interfaces. Surface chemical modification of straw fibres was carried out by poly(methyl hydrogen siloxane) (PMHS) to enhance compatibilization. Dried straw fibres were grafted with PMHS and then melt blended with polypropylene. All treatments even at low degrees of grafting significantly changed the hydrophilic nature of the straw fibres surfaces to hydrophobic one and improved the wettability of the straw fibres by the matrix which lead to improved adhesion. The rheological and morphological properties of composite were studied and results show that at low loadings, the viscosity of the treated straw fibres composite is reduced because of low molecular weight of PHMS. Water absorption of treated and untreated straw fibres was studied and results indicated the enhanced improvement in hydrophobic nature of treated fibres. Untreated and treated straw fibres with different amount of coating were floated on water for 2 h, results show that the water absorption is minimum in straws treated with 2 wt% of each PMHS and catalyst.

Key Words:

straw fibre;
polypropylene;
poly(methyl hydrogen siloxane);
PMHS;
compatibilization;
hydrophilicity.

INTRODUCTION

The physical properties of natural fibres are mainly determined by the chemical and physical compositions, such as fibre structure, cellulose content, degree of polymerization, angle of fibrils, and cross-section. Only a few characteristic values, especially the specific mechanical properties of natural fibres, can reach to comparable values of traditional

reinforcing fibres. The application of natural fibres as reinforcements in composite materials, similar to glass-fibre reinforced composites, requires adequate adhesion between the fibres and the matrix. This is true regardless of the application of a traditional polymer (thermoplastics or thermosets) matrix, a biodegradable polymer matrix, or cement. In addition,

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processing conditions play an important role in the industrial application of these materials.

The higher amount of natural organic reinforcements such as cellulose fibres is more and more used in plastic industry. The two main drawbacks of cellulose fibres as reinforcement for thermoplastic materials are:

- i) Relatively low degradation temperature (around 200°C).
- ii) Water sorption.

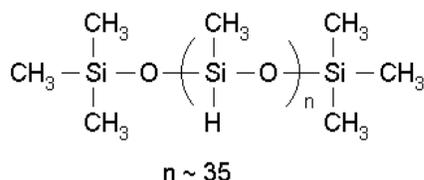
The first drawback limits variety of thermoplastic materials used as matrix which requires processing temperatures lowers than the degradation temperature of cellulose fibres.

The second one has adverse effect on adhesion to hydrophobic polymers. This is attributed to a variety of parameters including those commonly encountered with composite materials i.e., poor adhesion between the hydrophilic reinforcement and the hydrophobic polymeric matrix, (in the most general case), poor dispersion of the reinforcement within viscous polymeric matrix and poor wetting of the reinforcement surfaces by the polymeric matrix. There are several approaches for overcoming the above limitations [1-5].

Polymerization compounding (PC) was used by Hashemi et al. [6] as an approach aimed at overcoming the partial limitation in Kraft fibre composite. It consists of using the surfaces of the reinforcing material as supporting medium for polymerization. The synthesized polymer on the surfaces of the solid reinforcement will be used either as matrix in the final composite or as a special surface treatment.

In the latter case, the grafted polymer can be either identical or compatible with the matrix of the composite. This approach has been used with a variety of polymerization techniques and reinforcing agents by Salehi-Mobarekeh et al. [7-8], Brahimi et al. [9], and Casenave et al. [10].

In case of Kraft fibres, PC approach was the only



Scheme I. Chemical formula of poly(methyl hydrogen siloxane).

way to process such fibres because of non-disparity of fibres in matrix. In this case, we have used a coupling agent (PMHS) in order to change hydrophilic surfaces to hydrophobic ones. The PMHS approach is comparatively much cheaper in term of chemicals, time, and process than the one used for Kraft fibres [6] and with different fibres and matrix [6-10].

EXPERIMENTAL

Fibre Modification

Straw fibres were obtained from the market at different lengths, and then homogenized to the length of average 2.5 mm, in a plastic mill (Mini Grinder Electra, Japan) model EK-260G. In order to remove its smell the homogenized straw fibres were washed with water and detergent and the remaining detergent was removed by extensive washing with water. The washed straw fibres were air dried and then oven dried for a period of 4 h in an air circulating oven. The moisture was measured using the weight gain of the treated and untreated straw fibres floating in water. The poly(methyl hydrogen siloxane) which its chemical formula is shown in Scheme I was purchased from Dow. The dried product was mixed in jet mixer with 2 wt% of PMHS with addition of 2 wt% catalyst and cured in an air circulating oven for 3 h till the wetting was completed.

Compounding

Treated straws were further blended with propylene at 160°C in Haake internal mixer at concentration loading

Table 1. Effects of percentages of PHMS and catalyst on the water absorption of straw fibres.

No.	PMHS	Catalyst	straw	water absorption (%)	Drowing time (min)
1	0	0	100	5	5
2	1	1	98	4	20
3	1	2	97	4.2	25
4	2	1	97	0.7	25
5	2	2	96	0.3	1200
6	2	3	95	0.6	600
7	3	1	96	2	120
8	3	2	95	0.6	600
9	3	3	94	0.3	1200
10	4	3	93	0.3	1200
11	4	4	92	0.3	1200
12	4	5	91	0.3	1200

of 5, 10, 15, 20, and 30 wt% of straw fibres. Untreated dry straw fibres were also mixed in similar manner for comparison.

Rheological Testing

The compounds prepared in Haake internal mixer were compression moulded at 160°C, using a laboratory press (Mini Pestpress, 10 Poyosciti), into disks of 1.6 mm thickness and 25 mm diameter for rheological tests. The rheological properties were measured with a controlled stress rheometer, MCR300 Paar Physcia, using 25 mm diameter parallel plate fixtures. All tests were performed at 165°C. Time sweep tests were carried out on all samples to ensure that no thermal degradation occurred for the duration of the tests. The

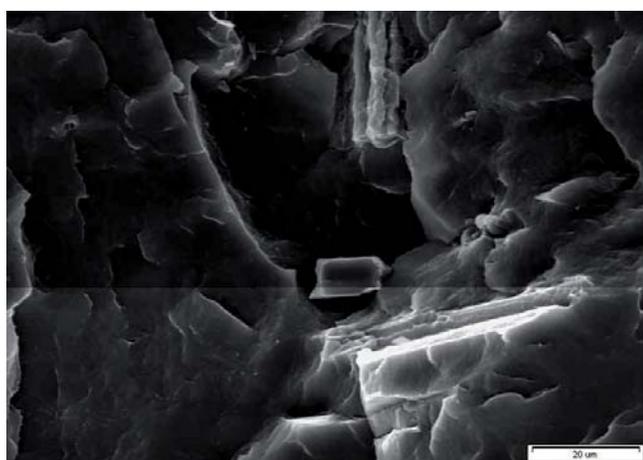
viscoelastic properties were determined in the linear domain for a strain of about 0.01 (corresponding to 5 - 1000 Pa).

Microscopic Observation

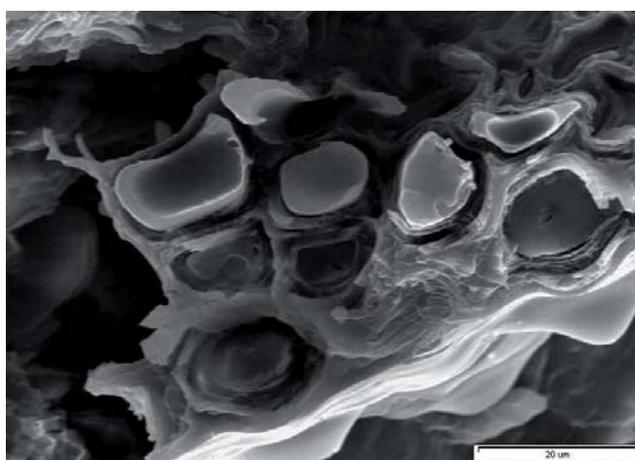
Scanning electron microscopy (SEM) model 360 Cambridge was used to investigate the interfacial properties. All surfaces were coated with a gold-palladium alloy under vacuum prior to investigation. Unmodified and modified straw fibres and surfaces of moulded samples were examined.

Water Absorption Measurement

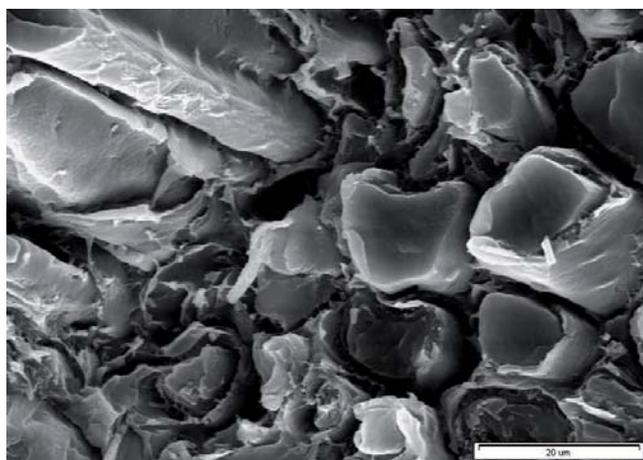
The straw fibres were treated with different amount of PHMS and catalyst. Fix amount of treated and untreated



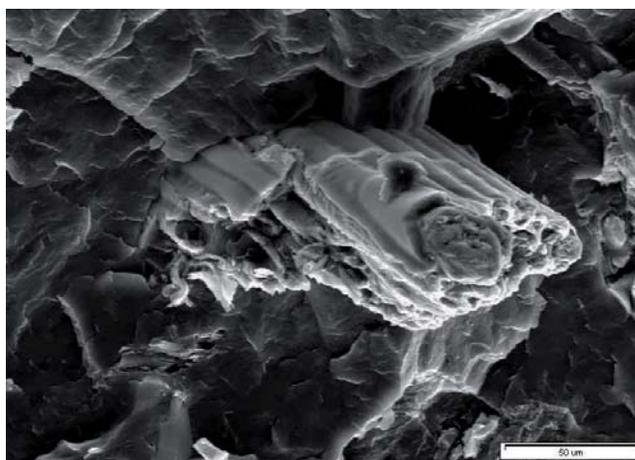
(a)



(c)



(b)



(d)

Figure 1. The SEMs of (a) 5 wt% (x500), (b) 10 wt% (x2000), (c) 15 wt% (x1500), and (d) 20 wt% (x1000) of untreated straw fibres in PP matrix.

straw fibres were weight and floated on water, the amount of water absorption versus different amount of coating agent and catalyst were measured.

RESULTS AND DISCUSSION

Table 1 demonstrates the effects of PMHS and catalyst concentrations on water absorption of straw fibres based on the results of the 2 wt% of each parameter for the optimum coating.

A first view of the effect due to the straw fibres treatment is offered in Figures 1 and 2 which compare the morphology of the fibres before and after modification. The morphology of the treated fibres has been changed in such a manner that they could be

protected against water and at the same time to ease the processing of fibres with polymer. Figures 1a-1d are SEM micrographs of the fibres before treatment and Figures 2a-2d are the corresponding micrographs after fibres have been coated by PMHS. A poor dispersion and no adhesion between the fibres and matrix are observed for the PP composite with untreated fibres (Figures 1a-1d). During the preparation of the composites under high shear conditions in Haake, it is assumed that the straw fibres can be considerably broken down in the case of untreated fibres. But in the case of treated fibres, the flexibility due to PMHS retains their sizes which this effect can not be seen by SEM.

Linear Viscoelastic Properties

The rheological properties of the straw fibres-PP

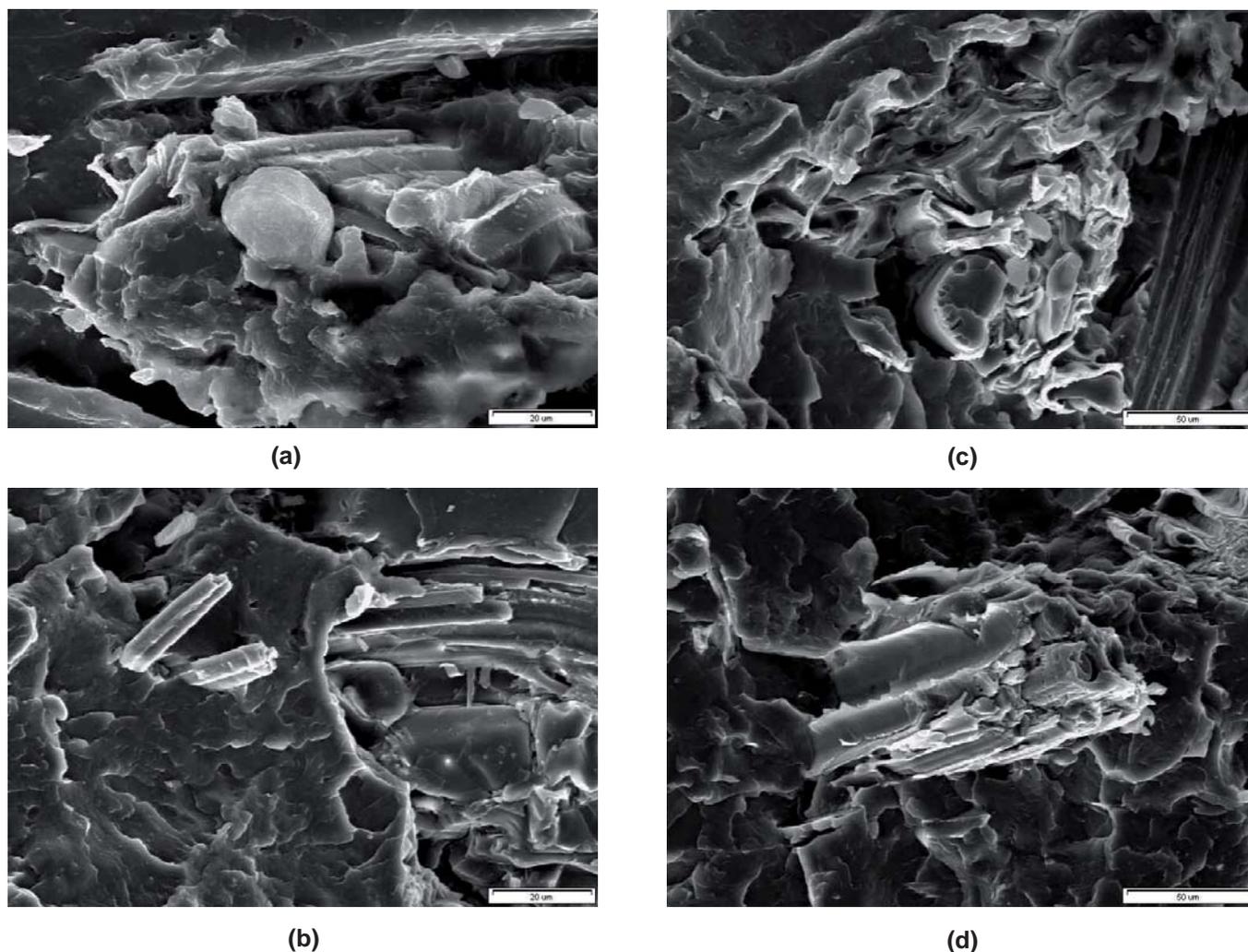


Figure 2. The SEMs of (a) 5 wt% (x500), (b) 10 wt% (x500), (c) 15 wt% (x1000), and (d) 20 wt% (x1000) of treated straw fibres in PP matrix.

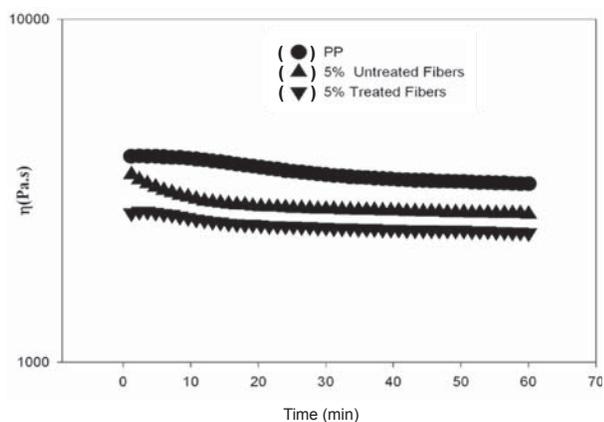


Figure 3. Thermal stability test for 5 wt% untreated and treated straw fibres-PP composites sample in term of viscosity.

composites were investigated since these are key factors in the optimization of injection moulding and other processing conditions. In general, the addition of fibres is known to affect the flow properties of composites, and this effect has been shown that is depended on the interfacial interaction and the degree of dispersion.

Thermal stability of composites was also studied at 165°C in order to understand the stability of composites for duration of frequency sweep test measurements. The straw fibre composites were found to be stable at temperature of 165°C and above, up to 200°C [6]. However, the thermal stability was excellent at 165°C for untreated and treated straw fibres loading up to 20 % as shown in Figures 3-5.

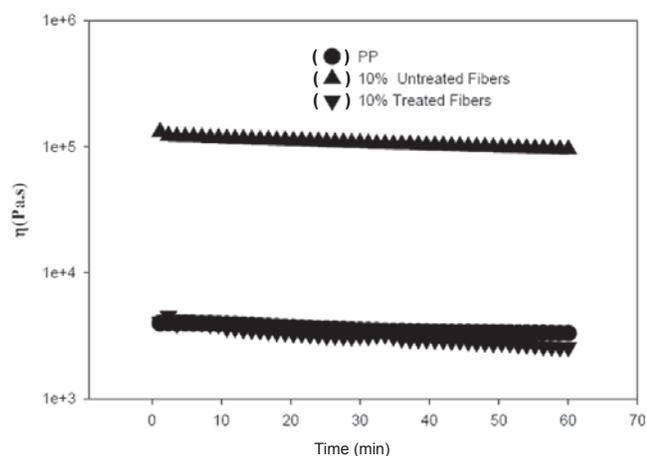


Figure 4. Thermal stability test for 10 wt% untreated and treated straw fibres-PP composites sample in term of viscosity.

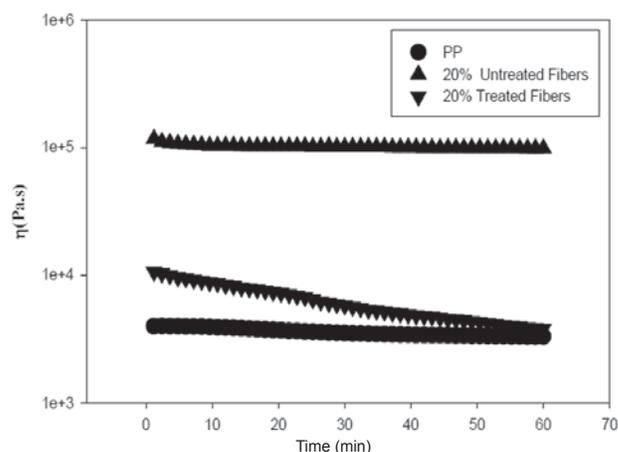


Figure 5. Thermal stability test for 20 wt% untreated and treated straw fibres-PP composites sample in term of viscosity.

Figure 6 shows that thermal stability of 30 wt% untreated straw fibres composite which its viscosity reduced below the viscosity of 30 wt% treated straw fibre composite; this effect is due to degradation of untreated straw fibres. Viscosity and loss modulus were calculated from frequency sweep test in linear region of 5-1000 Pa and are presented in Figures 7-10. The results show that the complex viscosity and loss moduli increase for untreated straw fibres composite with fibre loading content up to 20%. For the treated straw fibres these increases are not as much, compared to the untreated one. These differences in viscosity reduction of composites with treated constituents are viewed as the effects of coupling agent on the viscosities of

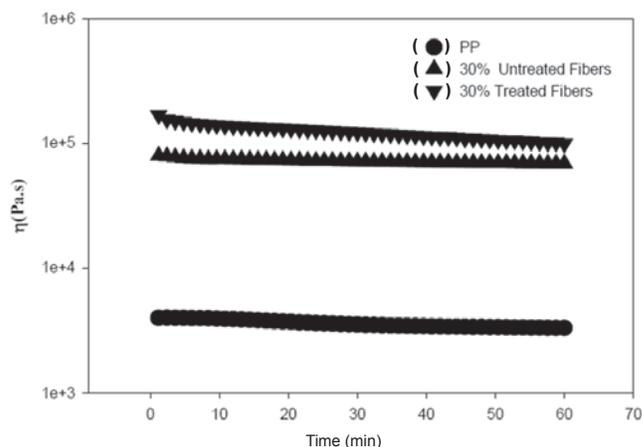


Figure 6. Thermal stability test for 30 wt% untreated and treated straw fibres-PP composites sample in term of viscosity.

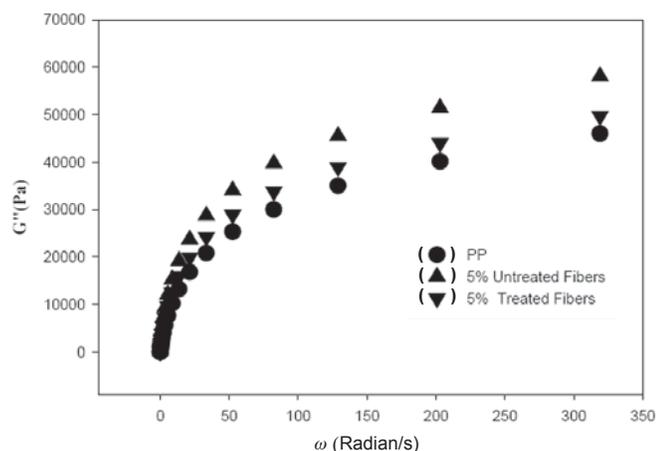


Figure 7. Comparison of storage modulus for 5 wt% untreated and treated straw fibres-PP composites from dynamic data.

the filled polymer [11-13]. Materials such as silanes enhance the adhesion at the polymer/filler interfaces, and in the process lower the melt viscosity, this effect has been shown on Kraft wood fibres[6].

Increasing straw fibres content results in an increase in the viscosity of both types of composites (Figures 7 and 8) for loading of 10 to 30% but reduced at loading of 5%. This is due to better dispersion and low molecular weight compound forming on the surface of straw fibres which acts as processing aid. The unmodified 5, 10 and 20% composites are found to have higher viscosity, over almost the whole range, than the corresponding ones prepared with modified fibres.

At loading of 30% straw fibres, the viscosity and loss modulus of untreated straw fibres are reduced

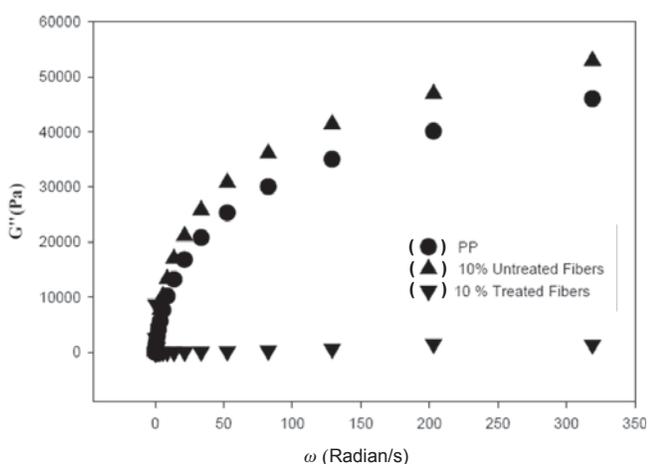


Figure 8. Comparison of storage modulus for 10 wt% untreated and treated straw fibres-PP composites from dynamic data.

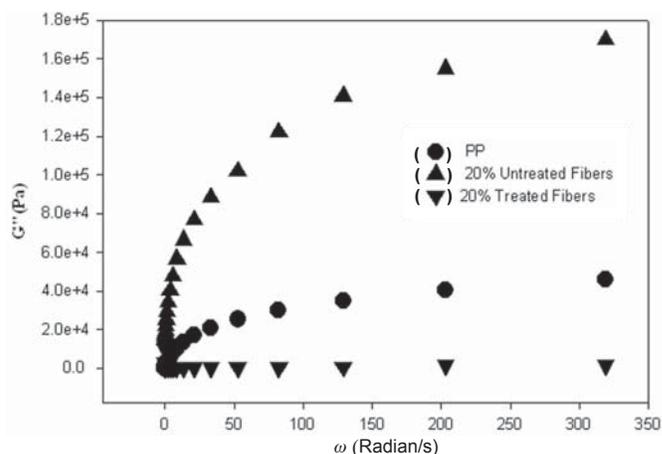


Figure 9. Comparison of storage modulus for 20 wt% untreated and treated straw fibres-PP composites from dynamic data.

which is the indication of straw fibres degradation. At loading of 30% straw fibres, the viscosity should increase and since the residence time increase and the straw is not a very good heat conductive material, the process of degradation start and therefore the viscosity is reduced.

In the case of treated straw fibres, coating acts as a good lubricant and processing aid which compensate the changes in viscosity. The PHMS act as protective coating which reduces the chances of straw fibre degradation compare to untreated one. These results are in agreement with those reported in the literature for fibre composites with different kinds of fibres (10,14,15).

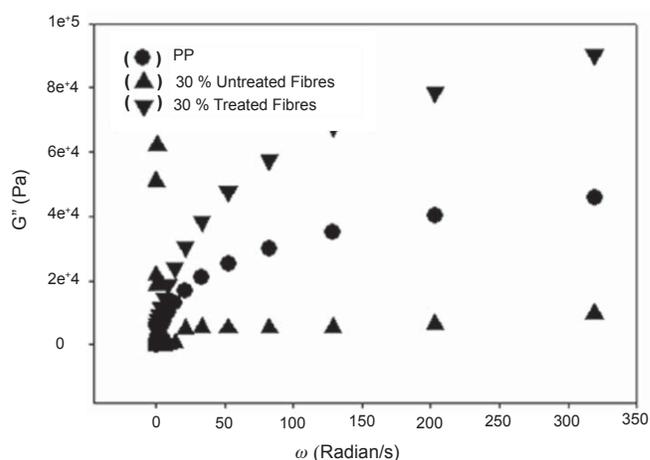


Figure 10. Comparison of storage modulus for 30 wt% untreated and treated straw fibres-PP composites from dynamic data.

CONCLUSION

compression moulded of PP composites with modified straw fibres were prepared. Fibre modification was carried out using PHMS approach. The straw fibre-PP composite containing 30 wt% straw fibre was obtained by this approach. All morphological and rheological data indicate the important effect of surface modification on properties of such composites. These changes are clearly seen by SEM and rheological properties. Rheological tests show that the viscosity of the modified straw fibre-PP composites increase as percentage of straw fibre increases. But compared with untreated straw fibre composites the viscosity increase is not as large as the viscosity change of untreated ones. This is due to the effect of coupling agent. Rheological properties have been improved due to interaction between polymer and straw fibres. Rheological results show that fibres coated with PHMS are thermally stable. There is an unusual reduction in viscosity of 30 wt% untreated straw fibres composite in term of thermal stability and sweep test which can be attributed to the degradation of straw fibres.

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