Evaluation of Dynamic Elastic Properties of Wood-Filled Polypropylene Composites

Shakti S. Chauhan, Ajay Karmarkar, Pankaj Aggarwal

Institute of Wood Science and Technology, Bangalore, India

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ABSTRACT: Dynamic modulus of elasticity (MoE) and shear modulus of wood-filled polypropylene composite at various filler contents ranging from 10% to 50% was determined from the vibration frequencies of disc-shaped specimens. Wood filler was used in both fiber form (pulp) and powder form (wood flour). A novel compatibilizer, *m*-isopropenyl-α,α-dimethylbenzyl-isocyanate(*m*-TMI) grafted polypropylene with isocyanate functional group was used to prepare the composites. A linear increase in dynamic MoE, shear modulus, and density of the composite was observed with the increasing filler content. Between the two fillers, wood fiber filled composites exhibited slightly better properties. At 50% filler loading, dynamic MoE of the wood fiber filled composite was 97% higher than that of unfilled polypropylene. Halpin-Tsai model equation was used to describe the changes in the composite modulus with the increasing filler content. The continuous improvement in elastic properties of the composites with the increasing wood filler is attributed to the effective reinforcement of low-modulus polypropylene matrix with the high-modulus wood filler. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 1706–1711, 2006

Key words: modulus; polypropylene; shear modulus; vibration; wood; wood–polymer-composites

INTRODUCTION

The use of natural fibers as fillers for thermoplastics has increased rapidly over the past decade, primarily due to environmental and economic benefits. Natural fibers are low-cost, low-density materials with high specific properties. They are also carbon dioxide neutral in their production (they derive carbon from air and not from oil or natural gas) and require only small energy inputs for processing. Because of these advantages, wood-filled composites are being increasingly used for building applications, such as outdoor decking, fences, window, and door frames.

Properties of wood fiber filled composites strongly depend on the process parameters and process formulations. Also, natural fillers exhibit large scatter in their properties, resulting in large variations in the properties of the final product. These variations demand for a fast and reliable method to assess properties of the composite material. For a homogeneous isotropic material, three important engineering elastic coefficients namely Young's modulus (E), shear modulus (G), and Poisson's ratio (ν) describe the elastic behavior. Out of these three, only two constants need to be determined and the third constant can be estimated from the other two using the following relationship:

$$G = \frac{E}{2(1+\mu)} \tag{1}$$

Studying properties of polymer materials by measuring the elongation, destructing stresses, and fatigue is very likely to be affected by changes in the structure, and consequently, in the properties of materials. This is the result of orientation and other effects due to the high value of the mechanical stresses appearing in the material and the relatively large strains.[1] Difficulties in accurate determination of static modulus of elasticity (MoE) have often been encountered due to the presence of nonlinearity in load–displacement curves.[2] Static tests also exhibit relatively large displacements over long test durations. All these make interpretation of the experimental data difficult and give ambiguous results.

Acoustic methods are one of the most studied and are extensively used to determine elastic constants, damping and attenuation characteristics, fatigue behavior, presence of flaws, and other defects in the materials nondestructively, including wood.[3–6] Among these, determination of elastic constants has received much attention due to the speed, accuracy, and convenience of the method. Dynamic modulus measurements occur over a very short duration and exhibit infinitesimally small displacements. This renders the

Correspondence to: S. S. Chauhan (shakti@iwst.res.in).

dynamic test relatively immune to the deficiencies associated with static tests.[2] Most often, bar-shaped (rectangular or cylindrical) samples are used for dynamic testing and longitudinal or flexural vibration frequencies are used to determine the dynamic MoE and torsional vibration frequencies are used for shear modulus determination.

In this article, we report elastic constants (MoE, Poisson's ratio, and shear modulus) determination of wood–polypropylene composites at different levels of wood content using disc-shaped samples. The advantages of using disc-shaped samples is that it provides a direct estimation of Poisson's ratio from the ratio of flexure and antiflexure frequencies unlike other methods where Poisson's ratio is estimated by combining separate measurements of Young's modulus (E) and shear modulus (G), which is inherently a less accurate method.

EXPERIMENTAL

Materials

Isotactic polypropylene (Repol H100EY), having a melt flow index of 11 g/10 min at 230°C under 2.16 kg load was procured from Reliance Industries, India. Dioctyl pthalate and zinc stearate (s.d. Fine-Chem, India) and Irganox B-215 (Hindustan Ciba-Geigy) were used as-received from the suppliers. Bleached kraft pulp of Eucalyptus was received as a gift from Mysore Paper Mills, Bhadravati, India. Wood flour was prepared from *Hevea brasiliensis* chips using a Frisch pulverizer with 0.5-μm-size mesh.

Composites preparation

A series of wood–polypropylene composites having 10, 20, 30, 40, and 50 wt % of wood fibers and wood flour were prepared in a twin-screw extruder. The extruder was having segmented screws and segmented barrel with six heating zones (Z1–Z6). Twin-screw extruders are most preferred for compounding because of their positive pumping action, efficient mixing, and shorter residence time. Both wood flour and wood fibers were dried at 105°C in a hot air circulated oven to a moisture content of less then 1%. Polypropylene homopolymer (3 kg), Irganox 1010 (15 g), dioctyl pthalate (7.5 g), zinc stearate (7.5 g), paraffin wax (7.5 g), and the compatibilizer, *m*-TMI-grafted-PP (5 wt % on fiber) were dry blended in a double cone blender. *m*-TMI-grafted-PP was synthesized by grafting *m*-isopropenyl-α,α-dimethylbenzyl-isocyanate (*m*-TMI) onto isotactic polypropylene (PP) in a twin-screw extruder. *m*-TMI (10% w/w) was absorbed on porous polypropylene granules and the mixture was fed through main hopper of the extruder at 50 g/min using a volumetric feeder. Dicumyl peroxide (10% w/w) was introduced through the side feeder. The reactive extrusion was performed by heating the extruder to the set temperature profile. The temperature of the feed zone, the mixing zone, the reacting zone, and the die zone of the extruder were set at 180°C, 190°C, 200 °C, and 180°C, respectively. The main screw was operated at 90 rpm. Under these conditions, the residence time of the material was about 4.5 min. When the set temperature was reached, the main drive of the extruder was started and the extruder was purged with nitrogen. The system was started with pure PP and the peroxide feed rate was gradually increased to the set value. After ~10 min, when steady state conditions were reached, the pure PP feed was changed to mixture of PP and *m*-TMI. The *m*-TMI-grafted-PP was collected by cooling the extrudate on a moving steel belt.

The polypropylene blended with process additives was fed through the main inlet hopper of the extruder. The wood flour/fibers were force fed into the molten polypropylene using a twin-screw side feeder fitted at a distance of about 19×screw diameter from the main inlet hopper and was located at Z3. The extruder rpm was about 150 and the extrusion temperature profile in six heating zones from Z1 to Z6 was set at 155°C, 180°C, 190°C, 195°C, 195°C, and 185°C.

Vacuum venting was used to remove the residual moisture and volatiles produced during WPC production. The product was recovered by guiding the molten extrudate into a standard cold water-stranding bath. The cooled strands were subsequently chopped into pellets, dried, and stored in sealed plastic bags.

Specimen preparation

The compounded pallets of wood polymer composites were molded into circular discs (100 mm diameter and 3 mm thickness) using an 80-ton Engel make microprocessor-controlled injection molding machine. After molding, the specimens were conditioned for at least 3 days before testing. For each composite formulation, five disc samples were taken randomly. Each selected sample was weighed to an accuracy of 0.001 g and measured for the dimensions (thickness and diameter) using a micrometer to an accuracy of 0.01 mm. Density of the composite samples was determined from weight and volume measurements.

Nondestructive testing

For a free circular plate or disc, there are two fundamental modes of vibration. One of the natural vibration mode has a nodal circle and the other has two mutually perpendicular nodal diameters.[7] The mode with nodal circle is termed as "flexure mode" and the other mode with two nodal diameters is termed as "antiflexure mode." The schematic diagram of exper-

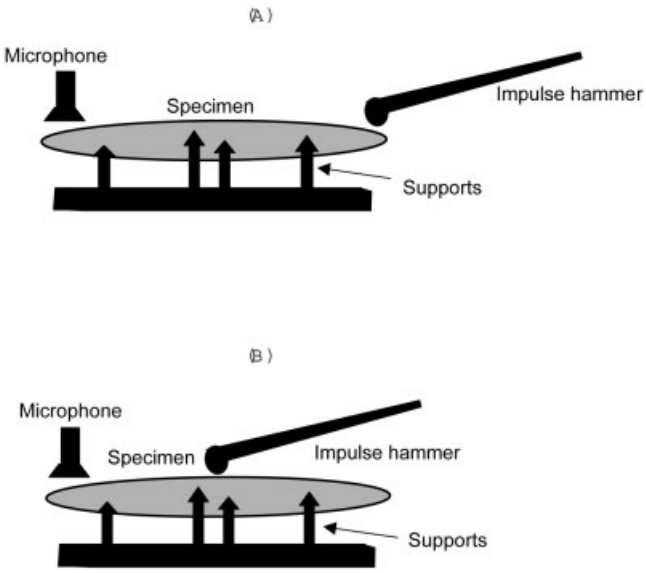

Figure 1 Experimental set-up for obtaining vibration frequencies of a disc (A) antiflexure mode (B) flexure mode.

imental set-up with the necessary support conditions and tapping positions for these modes are shown in Figure 1.

The discs were supported at four points located on two perpendicular diametral lines at 0.68×radius distance from the disc center to create a free–free support condition for both fundamental modes of vibrations. The support points were on nodal points of both the vibration modes. The edges of the plates were unbound. First the disc was tapped gently at the center. When struck at the center, an axisymmetrical, "diaphragm " mode results, with a circular node approximately at 0.68×radius. The induced vibrations were detected using a microphone and the natural vibration frequencies were determined using a Fast Fourier transform (FFT) frequency analyzer. Subsequently, the disc was tapped at the edge of the plate to excite antiflexure mode of vibration and corresponding vibration frequency was recorded. In both the cases, sample was struck in such a way that the force was enough to excite the desired vibrational modes and yet was gentle enough not to give much momentum that can displace the specimen as a rigid body. Frequency measurements were repeated five times on each sample. Every time the recorded frequency was exactly the same for a sample.

RESULTS AND DISCUSSIONS

Density and vibration frequencies (antiflexure and flexure modes) of the composites at various filler contents are shown in Table I. It is evident that all the three variables increased linearly with the increasing filler content. The density of the composite at 50% filler content (both fiber and flour filled composites) was about 17% higher than that of unfilled polypropylene. This increase in density can be attributed to the compacting or packing of wood fibers or flour in the matrix during injection molding (density of the wood cell wall material is about 1500 kg m^{-3}).

Frequency of both the vibration modes also increased with the increasing filler content. Frequency of the antiflexure mode (f_1) was distinctively lower than the flexure mode (f_2). However, the ratio of flexure to antiflexure frequency decreased with the increasing filler content. The ratio of these frequencies, coupled with the disc thickness to diameter ratio, gives Poisson's ratio, ν, through a nomogram or algorithm. The Poisson's ratio of the composite material was obtained from the nomogram given by Martincek.[8] The ratio of flexure and antiflexure frequencies in virgin polypropylene was 1.93 which corresponds to a Poisson's ratio of 0.45. The higher Poisson's ratio of polypropylene is due to its rubbery nature. With the increase in filler content, the frequency ratio decreased and correspondingly the Poisson's ratio also decreased. At 50% loading, Poisson's ratio of the composite material was 0.39. The lowering of Poisson's ratio with an increased fiber/flour loading can be attributed to the restraining effect of wood fibers/flour reinforcement on deformation.

Either of the two frequencies combined with the disc dimensions, Poisson's ratio, and mass gives MoE. The MoE can be determined using the following equation as described by Timoshenko[7]

TABLE I
Density and Vibration Frequencies of Wood-Filled Polypropylene Composites

	Wood fibre filled composite				Wood flour filled composite			
Filler content (%)	Density (kg/m^3)	f_1 (Hz)	f_2 (Hz)	f_2/f_1	Density (kg/m^3)	f_1 (Hz)	f_2 (Hz)	f_2/f_1
0	900	492	945	1.92	899	487	941	1.93
10	920	516	963	1.87	931	518	973	1.88
20	971	547	1011	1.85	970	527	995	1.89
30	993	576	1064	1.85	1008	564	1047	1.86
40	1059	618	1139	1.84	1040	575	1056	1.84
50	1080	638	1165	1.82	1085	607	1108	1.83

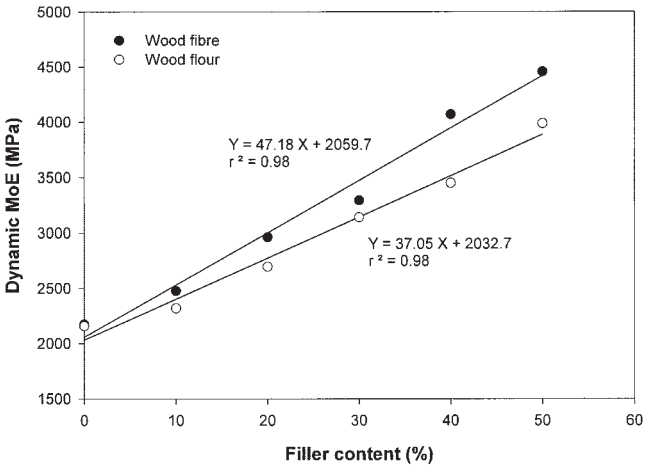

Figure 2 Variation in dynamic MoE with filler content.

$$\text{MoE} = \frac{3\pi^2 f_m^2 D^4 \rho(1-\mu^2)}{\kappa_{na}^2 t^2} \quad (2)$$

where D is plate radius, f_m is the vibration frequency (f_1 is the frequency of antiflexure mode and f_2 is of flexure mode), ν is the Poisson ratio, and t is the plate thickness. Values of κ_{na} depend on the Poisson's ratio and plate thickness to diameter ratio for the specific vibration frequency. Martincek[8] estimated value of κ_{na} for both antiflexure and flexure vibration modes for various plate thickness to radius ratio and various Poisson's ratio values. In case of unfilled polypropylene, κ_{na} values for antiflexure and flexure vibration mode were 4.75 and 9.13 respectively. There was no difference in the dynamic modulus obtained by using either of the frequencies with corresponding κ_{na} values. Dynamic MoE of the composite was determined using frequencies of second natural vibration mode, i.e., flexure mode for each formulation. Since the Poisson's ratio of the wood–polypropylene composite was varying with the filler content, value of κ_{na} for the flexure mode was derived for each composite formulation based on their Poisson's ratio.

Typical values of flexural modulus of virgin polypropylene used in this study (HO33MG and H100EY) are in the range of 1600–1700 MPa as provided in the product datasheet. The values indicated were from the static bending test (1% secant method) as per the ASTM standard. The dynamic modulus obtained from vibration frequency was 2160 MPa for HO33MG and 2174 MPa for H100EY. The difference between dynamic and static modulus has been attributed to the different loading rate and corresponding effect of creep in these two methods.[2,9] The dynamic modulus obtained for unfilled polypropylene was in close agreement with the storage modulus of PP at 30°C as reported by Harper.[10] Since the measurements are made using oscillation having small amplitude, the vibration frequency provides the actual information of the properties of the material, which do not change during the course of measurements.

Figure 2 shows the change in dynamic MoE of wood polymer composite with the filler content. A rapid increase in MoE was observed with increasing filler content. MoE at 50% filler content was 97% higher than that of virgin polymer in case of wood fiber filled composites and 85% higher in wood flour filled composites. Karmarkar et al.[11] have shown a linear increase in other mechanical properties like tensile and flexural strengths of the wood fiber filled polypropylene composites with a similar composite formulations. The improvement in strength properties was attributed to the increased interfacial adhesion and effective stress transfer from polypropylene matrix to fibers due to effective compatibilization of wood fibers with polypropylene matrix by *m*-TMI-grafted-PP as a compatibilizer. The continuous increase in dynamic MoE with the increasing filler content is primarily due to increased proportion and effective reinforcing of high-modulus wood material in the low-modulus polypropylene matrix.

Shear modulus of the composite material was estimated from the dynamic MoE and Poisson's ratio using eq. (1). Expectedly, shear modulus also increased with the wood filler content. For unfilled PP the shear modulus was in the range of 750–780 MPa which increased to 1400–1600 MPa at 50% filler loading (Fig. 3).

Wood fiber reinforced composites exhibited better dynamic MoE as compared to flour-filled composites at all the filler levels. The dynamic MoE of fiber-filled composite was about 12% higher than that of flour-filled composites at 50% filler content. This difference could be attributed to two factors. The first one is the difference in the aspect ratio of reinforcing material, i.e., pulp fiber length and wood flour length. In case of wood flour, wood was pulverized to the fraction of a millimeter, cutting

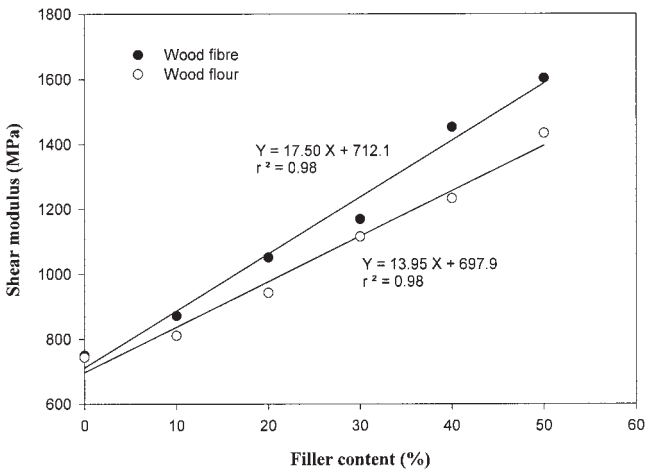

Figure 3 Variation in shear modulus with filler content.

down most of the fibers, while in case of wood fibers, a significant proportion of full-length fibers along with the fine fractions of eucalyptus pulp were blended with the polymer. The second factor might be the difference in the modulus of wood fiber and wood flour. Pulp fibers are relatively much stiffer than the solid wood. Thus reinforcing of polypropylene with stiff fibers would have resulted in higher dynamic MoE than with wood flour.

The effective change in the modulus of the composite material can be described by individual properties of filler, matrix material, orientation, and distribution of the filler material in the composites using empirical models. Halpin-Tsai model equation is one of the most popular models for describing the properties of composite material with randomly oriented filler or those having particulate or other nonfibrous reinforcements.[12] The model equation can be written in the following form:

$$E_c = \frac{E_m[E_f + \Phi(V_f E_f + V_m E_m)]}{V_f E_m + V_m E_f + \Phi E_m} \quad (3)$$

where E_c, E_m, and E_f are the Young's modulus of the composite, matrix, and filler material respectively, V_f is the volume fraction of filler, V_m is the volume fraction of matrix, and Φ is an adjustable parameter that depends on the orientation of the reinforcing material in the composite. The value of Φ is zero when the stress is applied in the direction perpendicular to the fibers and very large when load is applied parallel to the fiber orientation.

The MoE of the prepared composite material was predicted using the model equation. MoE of unfilled polypropylene was taken as the modulus of matrix. In case of wood flour filled composite, modulus of filler material was considered to be 10 GPa (MoE of rubber wood). For wood fiber filled composite, the modulus of the eucalyptus pulp was considered to be about 35 GPa. The value of Φ, an adjustable parameter, was assumed to be 1.5. A low value of Φ is justifiable as most of the filler material is expected to get oriented along the disc diameter during injection molding (perpendicular to the applied load) and a very small fraction of particles or fibers remains along the thickness of the circular plates (parallel to the applied load) due to "fountain effect" as described by Clemons et al.[13] The model predicted MoE were in good agreement with the experimentally determined MoE at all the filler loading levels (Fig. 4). The percent difference between observed and model predicted value was $\pm 6\%$ in all the cases expect at 50% wood fiber loading where the difference was about 12%. Kalaprasad et al.[12] have also shown a good agreement between experimentally

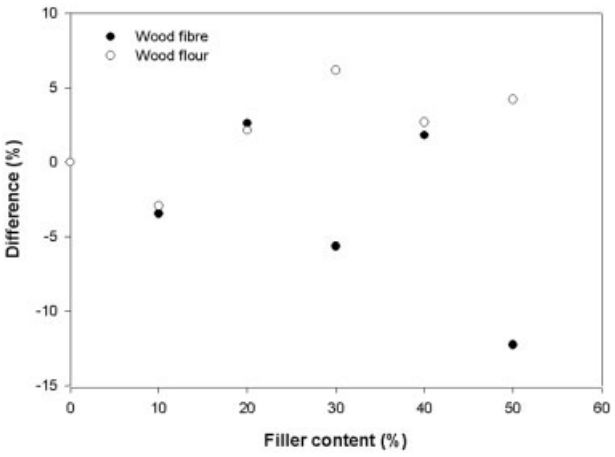

Figure 4 Difference (%) between experimentally observed and model-predicted MoE.

observed and model-predicted Young's modulus values in sisal fiber-filled low-density polyethylene composites particularly at low volume fraction of fibers. This was primarily attributed to the proper orientation and even dispersion of fibers resulting in uniform distribution of the load at low fiber content in the randomly oriented composites. The results suggested the suitability of Halpin-Tsai model in predicting MoE of wood–polymer composites from the individual modulus of wood and polymer.

CONCLUSIONS

Natural vibration frequencies of disc-shaped specimens were used to assess MoE and shear modulus of the wood-filled polypropylene composites at different filler content level. The disc-shaped specimens provided a direct estimate of Poisson's ratio from the ratio of flexure to antiflexure vibration mode frequencies. A significant improvement in density, dynamic MoE, and shear modulus was observed in wood-filled polypropylene composites with the increasing wood content. The improvement in modulus was nearly 100% as against 17% improvement in density at 50% filler loading. The dynamic MoE of wood fiber and flour filled composite was 4456 and 3987 MPa respectively, at 50% filler content as compared to 2170 MPa of unfilled polypropylene. Higher aspect ratio in wood fiber resulted in better MoE over wood flour. The continuous improvement in MoE is attributed to the reinforcement of low-modulus polypropylene with the high-modulus wood. The changes in the modulus of the composites with the change in filler content were further explained using Halpin-Tsai model. Model-predicted values were in close agreement with the experimentally observed values.

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