

Poly(vinyl chloride)–Acacia Bark Flour Composite: Effect of Particle Size and Filler Content on Mechanical, Thermal, and Morphological Characteristics

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ABSTRACT: This article describes the effect of filler [obtained from bark of Acacia (Babool)] content and its particle size (ranging from 100 to 150 μm and $<50 \mu\text{m}$) on the properties of poly(vinyl chloride) (PVC) composites. Bark of the fast-growing species Acacia was used as powder for making PVC composites, which may find applications as a substitute to high-cost wood and to avoid deforestation. A two-roll mill was used for mixing varying amounts of bark flour with PVC formulation. Samples for testing were prepared by compression molding. Tensile strength and percentage of elongation at break decreased, whereas modulus increased with an increasing amount of

bark flour. A significant increase in storage modulus (E') was observed upon incorporation of filler. Improvement in properties was significant in the presence of filler, having a particle size $<50 \mu\text{m}$ as compared to filler, having a particle size ranging from 100 to 150 μm . Morphological characterization was conducted by using scanning electron microscopy. A uniform dispersion of filler was observed in PVC matrix. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1309–1318, 2010

Key words: composites; poly(vinyl chloride) bark flour; morphology; particle size; renewable resources

INTRODUCTION

In recent years, wood-derived fillers have made significant contributions to the thermoplastic industry, which has led to the emergence of wood–plastic composites (WPC) in the construction industry. Products such as decking, fencing, siding, window framing, and roof tiles are being introduced into the market. It was predicted that for building products alone, ~ 1.1 billion pounds (500,000 tons) of WPCs was used in North America in 2006,¹ and this figure is increasing globally. The uses of wood–plastic composites are also increasing in construction, transportation, industrial, and consumer industries.

Growing interest of renewable resources based products is due to social and environmental concern. Natural fibers have several advantages, such as being inexpensive, being renewable, being lower density, undergoing little damage during processing, and their disposal causing minor ecological impact.^{2,3} Commodity thermoplastics such as polyethylene,⁴ polypropylene,⁵ poly(vinyl chloride) (PVC),^{6–12} and polystyrene are more commonly used in the manufacture of plastic/wood fiber compo-

sites. Such composites have lower material cost but higher stiffness than neat plastics.¹³

Mechanical and physical properties of natural polymer composites depend on various parameters such as volume fraction, aspect ratio, fiber orientation, dispersion level, polymer adhesion, mixing time, and processing conditions. Most studies involved the investigation of the mechanical properties of natural fiber-based polymer composites in terms of surface treatment^{14,15} and natural fiber content. Areas for improvement of PVC/wood flour composites still require much attention, especially in terms of thermal stability-related mechanical properties of the composites. Reports are available using wood flour as a filler for developing wood plastic composites; however, the use of bark flour in polymer matrix is not well investigated. The rise in resin prices are affecting all composite manufacturers by squeezing margins, which in turn force companies to reduce cost at all levels. Therefore, they need such filler/reinforcing material that can reduce the cost of manufacturing and simultaneously improve mechanical and thermal properties. The wood bark contains lignin, hemicellulose, and other extraneous materials (e.g., phenols, lignin, fatty acids, resins), which contain hydroxyl, carboxylic, ether, and phenolic functional moieties.^{16–18}

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An alternative to using bark as a source of chemical has been the pressing of bark fragments together to make bark-based composites.¹⁹ The incorporation of bark along with wood in particle boards has also been studied. Generally, as bark usage increases, particle board strength decreases.²⁰ Bark of *Acacia mearnsii* (Black Wattle) is a major source of vegetable tannin used in the manufacture of leather goods and adhesives.²¹

Bark exhibits heterogeneous structure and chemically it is very diverse in nature

	Wood	Bark
Lignin ^a	25–30	40–55
Polysaccharide ^a	66–72	30–48
Extractives	2–9	2–25
Ash ^a	0.2–0.6	Up to 20

^a Based on extractive-free material.

A survey of the *Acacia tannin* literature indicates the wide interest in tannin-based adhesives for the composite wood industry.^{22–24} *Acacia* species have been studied and used for pulpwood in many countries like Australia, Brazil, South Africa, Indonesia, Vietnam, and Malaysia.²⁵

Surplus bark is currently the most perplexing residue problem facing the wood conversion industries. The volume of bark residue is so great that it must be continually removed from mill sites. New technology has developed methods for converting slabs and edgings from a liability to an asset, and now utilization of bark is receiving increasing attention. Bark has useful byproducts waiting for the right economic conditions or the development of satisfactory commercial processes.

A survey of the literature reveals that the effect of bark flour on the polymer matrix has not been studied adequately. Only a few studies have been reported on the effect of bark flour and polymer matrix interaction.^{26,27} It was therefore considered of interest to investigate systematically the incorporation of bark flour on the properties of PVC. *Acacia* is a genus of about 800 species of deciduous and evergreen shrubs and trees. About 25 species are of Indian origin. *Acacia* is derived from Greek word “akis,” which means a sharp point. *Acacia* belongs to family Fabaceae.

The present article describes the effect of particle size and filler contents (bark flour) on PVC composites. Flour from bark of the fast-growing species *Acacia* was taken because this plant is found in abundance in India. Several samples were prepared by mixing bark flour with stabilized PVC formulation by using a two-roll mill followed by compression molding. The effect of filler content on static stability, mechanical properties, thermal stability, and morphology were investigated.

MATERIALS AND METHODS

Materials

PVC (trade name SR-10A), having molecular weight of K-67 (as Fikentscher K-value²⁸, Delhi, India), was procured from DCM Shriram Consolidated. Lead stearate was used as a heat stabilizer. Acrylic impact modifier, supplied by Rohm and Hass (USA), and calcium carbonate were used in making the PVC compound.

Bark flour was prepared by grinding the dried bark collected from the *Acacia* plant, followed by sieving using standard mesh to get the particle size <150 μm and <50 μm . Particle size was measured by using a particle size analyzer (Model CIF 100; Ankersmid, Italy) by suspending a small amount of powder bark flour in distilled water/glycerol. Two different bark flours having particle sizes 100–150 μm and <50 μm were used to make composites.

Preparation of composites

Bark flour was vacuum dried at 80°C for 24 h before blending. The dry PVC compound and required amounts of vacuum-dried filler were mixed by using a high-speed mixer (Sumit) in a grinder for 10 min. Several compounds were prepared by mixing PVC compound with varying amounts of filler ranging from 10 to 40 phr. The dry-blended compound was further mixed at 150°C using a hot-roll mill (Troester roll mill) to obtain leather hide having uniform dispersion.

Sheets for testing were prepared by compression molding. The pressing cycle was 10 min at 180°C. To have a similar thermal history, PVC compound was also subjected to the same processing conditions.

PVC compound blended with bark flour having particle sizes of 100–150 μm have been designated as PVC-WF followed by numerals indicating amount (in phr) of filler. For example, PVC having 10, 20, 30, and 40 phr of bark wood flour have been designated as PVC-WF10, PVC-WF20, PVC-WF30, and PVC-WF40, respectively. Similarly, the samples prepared by using 10, 20, 30, and 40 phr of bark wood flour of particle size <50 μm have been designated as PVC-NWF10, PVC-NWF20, PVC-NWF30, and PVC-NWF40, respectively.

Characterization

FTIR spectroscopy

The FTIR spectra of bark flour, neat PVC, and PVC–bark flour composites were recorded by using a Shimadzu FTIR 8700. Required amounts of dried sample and KBr were mixed thoroughly and pressed into a pellet by using a hydraulic press. The

resolution was 4 cm^{-1} and spectra were recorded in the range of $4500\text{--}400\text{ cm}^{-1}$.

Water uptake

Water uptake in PVC and PVC–bark flour composites was determined according to ASTM Standard D 570-99. For each composite, three rectangular ($63 \times 12.6 \times 2.2\text{ mm}^3$) pieces were cut from the compression-molded sheets and immersed in distilled water at 25°C . After 24 h of immersion, samples were taken out, wiped with filter paper to remove the surface water, and weighed again. The water uptake was calculated by using the following equation

$$\text{Water uptake (\%)} = \frac{W_1 - W_0}{W_0} \times 100$$

where W_1 is the weight of sample after immersing in water for 24 h (g); and W_0 is the initial weight of sample (g).

Specific gravity

Specific gravity was determined in accordance to ASTM D 792. The weight of the specimen in air and water was noted and density was determined.

Mechanical properties

Tensile properties were measured (25°C , relative humidity = 65%) by using a Zwick Universal testing machine Model Z010 in accordance to ASTM D 638. Dumbbell-shaped specimens were punched from the compression-molded sheets. A crosshead speed of 500 mm/min and gauge length of 65 mm were used in each experiment. Five specimens of each formulation were tested and the average value was reported.

Shore D hardness

Shore D hardness was determined by using Atsfaar (model REX-3102, Italy) in accordance with ASTM D 2240. The specimen, having a thickness of 6.4 mm , was placed on a hard, flat surface. The indenter of the instrument was then pressed onto the specimen, making sure that it was parallel to the surface. The hardness was read after 15 s of firm contact with the specimen.

Impact strength

Reversed notched izod impact strength was measured according to ASTM D 256, using a Ceast Resil

impact tester. The specimen was held in a vertical cantilever beam, broken by a pendulum. The specimen was impacted on the side opposite to the notch. The notch was formed at 45° with a depth of 2.45 mm .

Static thermal stability

Static thermal stability was determined according to IS 5831-1984. For this purpose, a weighed amount of sample (0.05 mg) was taken in the test tube, which was placed in a heating chamber maintained at 200°C . The time required to change the color of Congo red paper kept at the mouth of the tube was noted as stability time.

Thermal analysis

Differential scanning calorimetry

TA Q-10 thermal analyzer having a DSC module was used for recording DSC traces in nitrogen atmosphere. A heating rate of 10°C/min and a sample size of $5 \pm 2\text{ mg}$ were used in each experiment.

Thermogravimetric analysis

A Diamond-made simultaneous thermogravimetric analyzer-DSC-differential thermal analysis (DTA) [simultaneous differential thermal analysis (SDTA)] Perkin–Elmer system was used to record thermogravimetric traces in nitrogen atmosphere. A heating rate of 20°C/min and a sample size of $5 \pm 1\text{ mg}$ were used in each experiment.

Dynamic mechanical thermal analysis

Viscoelastic properties, such as storage modulus (E'), loss modulus (E''), and mechanical damping parameter ($\tan \delta$), as a function of temperature were measured by using a Rheometric Scientific DMTA (Model DMTA-IV). Rectangular bars having dimensions of $24\text{ mm} \times 5.8\text{ mm} \times 2\text{ mm}$ were used in a single-point bending mode. DMTA scans were recorded at an oscillation frequency of 1 Hz , strain 1% in the temperature range of $40\text{--}150^\circ\text{C}$. A heating rate of 3°C/min was used in each experiment.

Morphology

Fractured surfaces of the composites were used for morphological characterization by using a scanning electron microscope operated at 15 kV . The fractured surfaces were coated with a thin layer of gold and then images were recorded by using a Zeiss EVO 50 scanning electron microscope.

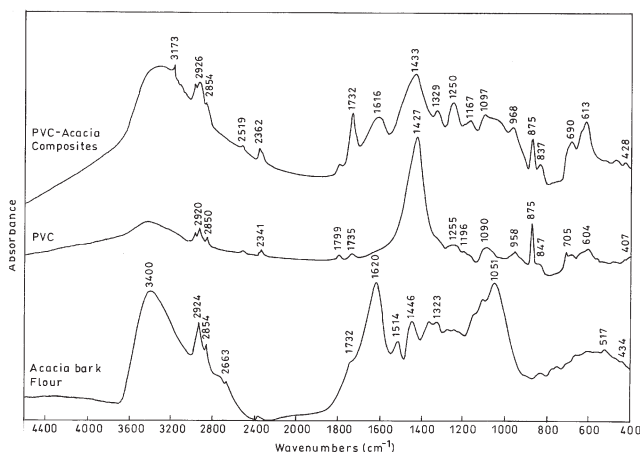


Figure 1 FTIR spectra of Acacia bark flour, PVC, and PVC-bark flour composite (measured by using KBr pellet technique).

RESULTS AND DISCUSSION

FTIR spectroscopy

Figure 1 shows FTIR spectra of bark flour, neat PVC, and PVC-bark flour composite. The assignment of peak for Acacia bark flour revealed broad stretching intermolecular bonded hydroxyl group at 3400 and C—H stretching around 2900 cm^{-1} . In the fingerprinting region between 1800 and 900 cm^{-1} , many sharp and discrete absorption bands due to various functional groups present in the bark flour were observed and the assignment was done as reported in the literature.²⁹ FTIR spectrum of neat PVC showed the two following characteristic bands: a very broad band at 702 cm^{-1} , probably due to C—Cl stretching, and a sharp band at 1427 cm^{-1} , due to the C—H group.^{30,31} The bands at 1735 and 1799 cm^{-1} due to the carbonyl groups were also observed in the FTIR spectrum of PVC, which could be due to the presence of some oxygenated structure in PVC. Similar behavior has been reported.³² In contrast, FTIR spectra of composites showed a dramatic increase in the peak intensity at 1732 cm^{-1} . The presence of cellulose is obvious from the very intense and sharp peak that appears at 1732 cm^{-1} . This is due to the stretching vibration of the carbonyl groups (C=O).³³ Because bark flour contains oxidized compounds such as carbonyl groups, the increase in the relative intensity of C=O stretching band at 1732 cm^{-1} provided good evidence of the incorporation of carbonyl group into the PVC matrix. The peak at 1166 and 1097 cm^{-1} is assigned to the ether linkage (C—O—C) from lignin or hemicelluloses.

Water absorption

The results of percentage of water uptake in PVC, PVC-bark flour (particle size ranging from 50 to 150 μm) composites are given in Table I. The water

uptake of the wood flour based composites largely depends on the availability of the hydrophilic groups (i.e., presence of free —OH and —COOH groups on the surface of the reinforcing wood flour). In all the samples, water uptake was in the range of 0.02–0.98%. A marginal increase in water uptake was observed on incorporation of filler. This behavior is totally predictable because PVC is hydrophobic, whereas wood flour is hydrophilic. As expected, water absorption increased with increasing amount of the wood flour content in composites; however, it was less than 1% even at a filler loading of 40 phr.

Specific gravity

Specific gravity of PVC and PVC bark flour composites was in the range of 1.44 ± 0.01 (Table I). Density of composites does not change upon incorporation of varying amounts of filler having particle size ranging from 50 to 150 μm .

Mechanical properties

Table II summarizes the mechanical properties of PVC bark flour composites at different loading of filler of varying particle size. Mechanical properties depend on various factors like filler content, particle size and shape, degree of adhesion between filler and the matrix, and filler dispersion in the polymer matrix. Tensile modulus of PVC-NWF composites was almost double as compared to PVC-WF composites at equal loading. As the filler content increased, modulus decreased from 293 to 205 in PVC-NWF composites, whereas in the case of PVC-WF, it decreased from 142 to 132. The decrease in tensile modulus at higher loading of filler can be attributed to the poor dispersion of the bark flour particle in the PVC matrix. Increasing the filler loading

TABLE I
Details of Sample Preparation and Results of % Water Uptake and Specific Gravity in PVC /PVC-Bark Flour Composites

Sample designation	PVC	Bark flour	% Water uptake (after 24 h of immersion at 25°C) (ASTM D 570-99)	Specific gravity (ASTM D 792)
PVC	100	0	0.02	1.44
PVC-WF10	100	10	0.11	1.43
PVC-WF20	100	20	0.25	1.43
PVC-WF30	100	30	0.29	1.43
PVC-WF40	100	40	0.98	1.43
PVC-NWF10	100	10	0.10	1.44
PVC-NWF20	100	20	0.16	1.44
PVC-NWF30	100	30	0.24	1.44
PVC-NWF40	100	40	0.41	1.45

PVC-WF and PVC-NWF represent composites of PVC having bark flour particle size 100–150 μm and <50 μm , respectively.

TABLE II
Mechanical Properties of PVC/PVC-Bark Flour Composites

Sample designation	Shore D hardness ASTM D 2240	Static thermal stability (min) IS 5831-1984	Modulus (MPa) ASTM 638	Tensile strength (MPa) ASTM 638	Elongation at break (%) ASTM 638	Impact strength (Rev. Notch) kJ/m ² ASTM D 256
PVC	71	55	172.6	45.9	38	Not break
PVC-WF10	75	35	142.0	43.2	5	12.0
PVC-WF20	76	33	123.8	37.8	3	5.6
PVC-WF30	77	32	137.8	34.2	3	4.2
PVC-WF40	77	31	132.5	30.1	3	3.1
PVC-NWF10	76	40	293.1	41.4	16	20.7
PVC-NWF20	77	36	252.0	40.5	4	9.7
PVC-NWF30	78	33	249.0	40.4	4	6.4
PVC-NWF40	78	30	205.0	40.4	3	4.2

PVC-WF and PVC-NWF represent composites of PVC having bark flour particle size 100–150 and <50 μm , respectively.

automatically increased the interfacial defects in the PVC matrix, which resulted in a decrease in composite homogeneity, and thus, caused poor stress transfer between the polymer matrix and the fiber.³⁴ The modulus was higher in PVC-NWF composites as compared to PVC-WF composites. This could be due to better reinforcing action of the microfiller. Similar behavior has been reported by several authors with different matrices.^{35,36}

As expected, hardness of PVC bark flour composites increased upon addition of filler. The addition of macro-sized filler (100–150 μm) had little affect as a function of concentration, whereas in composites having micro-sized (<50 μm) filler particles (NWF), hardness of the composites increased (Table II). The size and dispersion of filler particles in the matrix can affect the composite properties. Small, well-dispersed particles generally give better properties.³⁷ Smaller particles can block crack propagation, resulting in impact toughening. Hardness of the composites decrease with an increase in the volume

fraction of large-sized particles, while the hardness did not change with increasing volume fraction of micro-sized filler.

Tensile strength decreased with increasing amount of filler. This could be due to the poor dispersion of bark flour in the PVC matrix and the increase of interfacial defects or debonding between polymer and filler. Feldman and Banu³⁸ reported the existence of proton donor–proton acceptor interactions between hydroxyl or carbonyl groups of lignin and $\alpha\text{-H}$ of PVC. Bark flour, on the other hand, contains only a small fraction of lignin and very little may be distributed on the surface of the filler particles. Consequently the effect of the aforementioned interaction on the mechanical properties of wood flour filled PVC composites may not be so pronounced. It can be seen from Table II that tensile strength for PVC/WF composites decreased from 43 to 30, whereas in the case of PVC-NWF composites, it decreased marginally and showed no change with increasing amounts of filler.

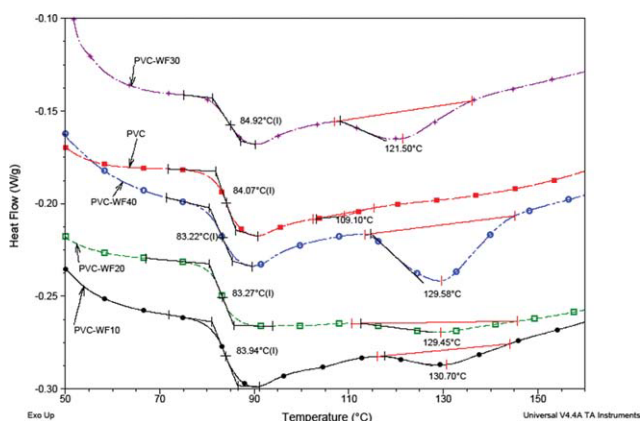


Figure 2 DSC spectra of PVC-WF composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

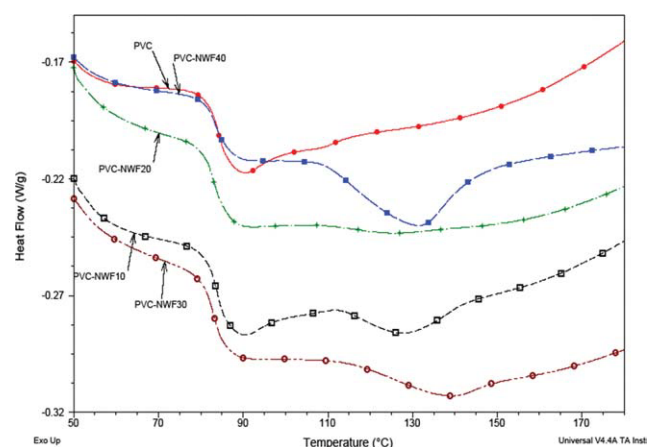


Figure 3 DSC spectra of PVC-NWF composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
Thermal Properties of PVC Compound, PVC-WF and PVC-NWF Composites

Material	T_g (°C)	T_m (°C)	Heat of fusion ΔH (J/g)	Temperature (°C)	T_{max}^1 (°C)	T_{max}^2 (°C)
PVC	84.0	109.1	0.044	103.0	301.5	464.2
PVC-WF10	83.9	130.7	0.73	117.5	313.0	466.2
PVC-WF20	83.2	129.4	0.57	112.5	309.3	469.4
PVC-WF30	84.9	121.5	1.38	108.1	306.4	468.3
PVC-WF40	83.2	129.5	2.95	114.5	304.5	468.0
PVC-NWF10	83.9	128.2	1.22	113.6	307.4	464.2
PVC-NWF20	83.5	125.2	0.32	109.8	308.2	469.4
PVC-NWF30	83.2	138.7	2.13	115.3	301.8	466.2
PVC-NWF40	83.71	131.6	3.97	109.0	298.6	461.9
Bark flour					310.0	—

PVC-WF and PVC-NWF represent composites of PVC having bark flour particle size 100–150 and <50 μm , respectively.

For polymeric composites, the addition of an immiscible component to polymer matrix generally decreases elongation properties considerably. As expected, a decrease in elongation at break for composites was observed having WF or NWF (Table II). These results clearly show that the presence of bark flour in the matrix reduces the ability of the sample to deform by restricting the mobility of the polymer chains. As a consequence, it is difficult for the segments of the material to easily slip past each other. For the composite containing NWF, there is a slight increase in elongation at break for the sample containing 10 phr of wood flour (i.e., sample PVC-NWF10). However, at higher loadings, no such difference was observed. This may be due to the uniform distribution of the wood flour having particle size <50 μm (i.e., NWF composites). Similar results were found by Anna et al.³⁹

Reverse notch impact strength is higher in micro-sized (<50 μm) filled composites as compared to macro-sized (100–150 μm) filled PVC bark flour composites at the same loading level. The larger particle size provides higher stress concentrations where a crack can be initiated more easily (i.e., less energy is required to initiate the crack) at low loading level (i.e., 10 phr more energy is required to break the sample).

Thermal behavior

Static thermal stability of PVC and PVC bark flour filled composites was determined by heating the sample at 200°C. Time taken by the Congo red paper to change its color due to evolution of HCl was used as a criterion for measuring thermal stability under isothermal conditions (Table II). The presence of bark flour decreased static stability and the time needed to change the color of Congo red paper decreased with increasing amount of bark flour. However, there was no significant difference in the presence of macro- or micro-sized filler.

Differential scanning calorimetry

Figures 2 and 3 show the DSC scans for the PVC, PVC-WF, and PVC-NWF composites. In the DSC scan of PVC, an endothermic shift in the baseline corresponding to T_g at 84°C and a melting temperature (T_m) at 109°C was observed. In the case of PVC-WF/PVC-NWF composites, T_g did not show (Table III) any change, indicating thereby the presence of two separate phases. It was an independent of amount of loading and size of bark flour used in composites. Similar results have been reported by Jiang and Kamdem.⁴⁰ In addition, the DSC scan of each specimen exhibited an endothermic transition ranging from 100 to 145°C with an endothermic peak designated as T_m (Table III). This endothermic region is attributed to the crystalline melting region of PVC.⁴¹ The increase in heat of fusion is more when we added the filler having particle size <50 μm , indicating that the crystallinity of the virgin matrix increased upon incorporation of filler having smaller particle size.

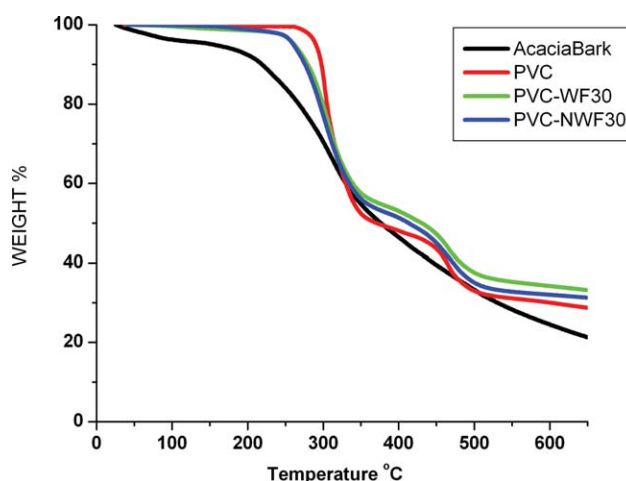


Figure 4 Thermograms of the PVC, Acacia bark flour, PVC-WF30, and PVC-NWF30 composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
Mass Loss and % Char Yield of PVC, Bark Flour and PVC-Bark Flour Composites

Sample designation	Decomposition temperature (°C) at % mass loss					% Char yield at 600°C
	10	20	30	40	50	
PVC	297.3	304.6	314.7	329.6	370.2	30.0
PVC-WF10	289.7	306.6	319.4	333.8	366.4	26.3
PVC-WF20	281.5	300.7	314.6	330.0	376.6	28.2
PVC-WF30	277.4	298.9	313.9	336.0	430.2	34.2
PVC-WF40	275.6	297.0	311.0	333.1	412.7	34.7
PVC-NWF10	279.5	297.7	311.7	327.0	371.4	26.3
PVC-NWF20	281.6	300.7	314.6	332.4	409.2	30.7
PVC-NWF30	275.7	294.4	310.5	334.1	413.0	31.2
PVC-NWF40	264.3	291.3	313.8	342.1	401.2	33.5
Bark flour	219	268.2	303.7	330.3	376.7	24.5

PVC-WF and PVC-NWF represent composites of PVC having bark flour particle size 100–150 and <50 μm , respectively.

Thermogravimetric analysis

The thermal stability of PVC–bark flour composites was investigated by using dynamic thermogravimetry in nitrogen atmosphere. Thermogravimetric traces for bark flour, PVC, and PVC–bark flour composites were recorded under identical conditions and the traces are shown in Figure 4. Bark flour showed a mass loss of $\sim 10\%$ up to 220°C, which may be attributed to the loss of water followed by major decomposition, leaving behind a char yield of $\sim 24\%$ at 600°C. Neat PVC and PVC-WF/PVC-NWF-filled composites showed a two-step degradation. Mass loss in the lower temperature region (due to moisture as observed in wood flour) was not observed in PVC-WF/NWF composites, indicating that the composites are hydrophobic in nature. Thermal stability of the sample was compared by noting the decomposition temperature at varying percentage mass loss (Table IV). Decomposition temperature at 50% mass loss was much higher (i.e., 43–

60°C) for composites having 30% w/w of wood filler as compared to neat PVC. It was higher in PVC-WF composites as compared to PVC-NWF composites. It is very difficult to determine the mechanism of degradation from decomposition profile. In the present work, this data are used as a measure of relative stability in the presence of filler.

At lower filler loading, percentage of char yield decreased, whereas it increased at higher loadings (i.e., 30 and 40 phr). Percentage of char yield observed at higher filler loading was higher than the values calculated by using the additively rule. Percentage of char yield was higher in the case of PVC-WF composites as compared to PVC-NWF composites (Table IV). From these results, it can be concluded that at higher loadings of filler, evolution of volatiles is hindered or mechanism of degradation has changed. The decomposition peaks in the derivative weight loss are designated as T^1_{max} and T^2_{max} and these correspond to the dehydrochlorination of the PVC matrix and to

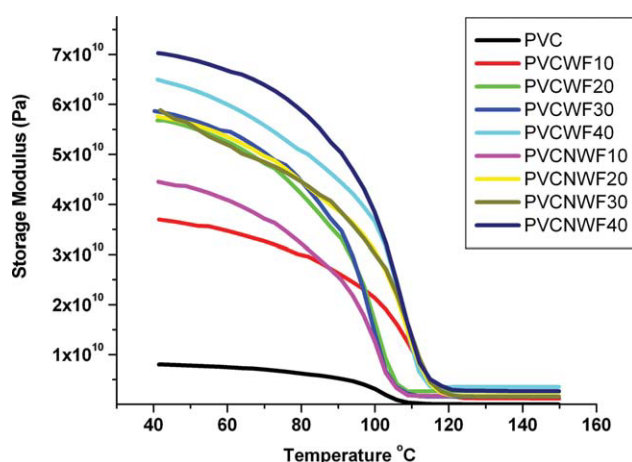


Figure 5 Storage modulus of PVC–bark flour filled composites as a function of temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

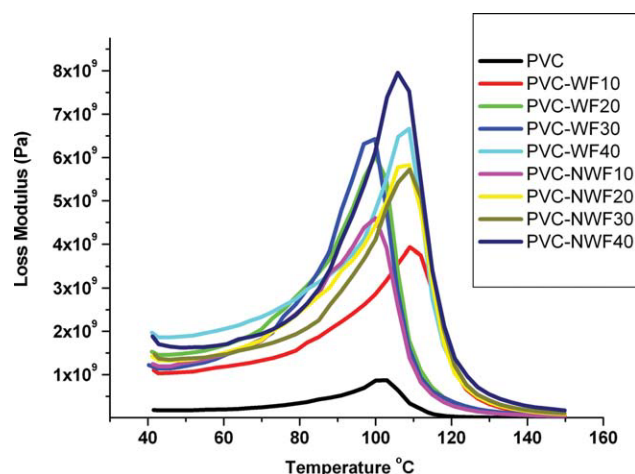


Figure 6 Loss modulus of PVC–bark flour filled composites as a function of temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE V
Glass Transition Temperature as Measured by Storage Modulus, Loss Modulus and Tan δ Peak

Sample designation	T_g from E'	T_g from E''	T_g from $\tan \delta$ peak
PVC	83.3	102.9	109.0
PVC-WF10	95.2	109.0	118.0
PVC-WF20	86.5	99.9	106.0
PVC-WF30	87.8	100.0	106.0
PVC-WF40	98.6	108.8	115.0
PVC-NWF10	86.2	100.0	106.0
PVC-NWF20	94.4	108.9	109.0
PVC-NWF30	92.0	109.0	118.0
PVC-NWF40	100	105.8	115.0

the thermal decomposition of polyenes (formed after dehydrochlorination of PVC), which consist mainly of conjugated double bonds, respectively.⁴²

Dynamic mechanical analysis

Figure 5 shows the variation of storage modulus (E') as a function of temperature for neat PVC and bark

flour filled PVC composites having different loadings of varying particle sizes. As expected, the storage modulus increased with an increasing amount of bark flour. Storage modulus of composite at a room temperature of 40°C at filler loading of 40 phr was significantly higher (7.02 GPa) than neat PVC (0.80 GPa). Substantial improvement in the rubbery plateau modulus of PVC bark composites over the neat PVC was clearly seen. These results clearly show that the addition of bark flour acts as a reinforcing agent for PVC matrix, thereby increasing the stiffness of the matrix. This was further supported by the increase in shore D hardness (Table II). Storage modulus is associated with the elastic response of the composites and indicates the stiffness of the materials. Being an inherent property of material, it is more associated with the molecular response and therefore can give a better estimation of the fiber-to-polymer matrix interaction. The increasing fiber concentration had increased the storage modulus of the composite because of the mechanical limitation posed by increasing fiber concentration embedded in

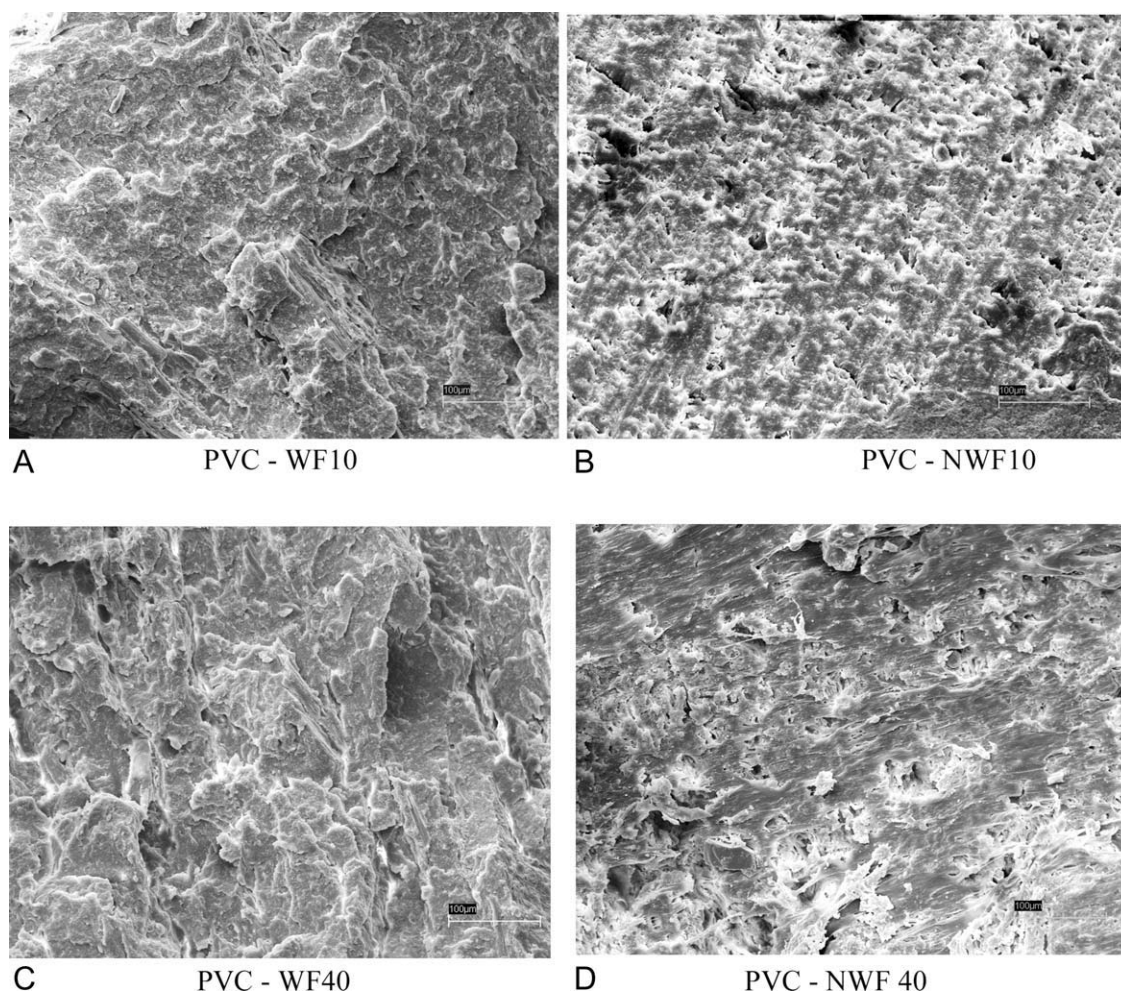


Figure 7 SEM micrographs of PVC bark flour filled composites having filler loading of 10 phr: (a) PVC-WF10, (b) PVC-NWF10 and filler loading 40 phr, (c) PVC-WF40, (d) PVC-NWF40.

the viscoelastic matrix, thereby reducing the mobility and the deformation of the matrix with increasing temperature.

Determination of glass transition is important for ascertaining the stability of the composites. There are different ways of determining glass transition temperature (T_g): shift or change in slope of E' (definition 1: transition from solid to rubber); peak of E'' (definition 2); and peak of $\tan \delta$ (definition 3: domination of liquid behavior over solid) are observed.⁴³ Figure 6 shows the plots of loss modulus vs temperature for PVC and PVC composites having varying amounts of bark flour. T_g was noted as the peak temperature. It increases with an increase in filler content. It is well reported in literature that the values obtained from storage modulus, loss modulus, or $\tan \delta$ plots differ to a significant extent.^{44,45} In the present article, T_g was noted as a peak temperature of loss modulus vs temperature or by drawing a tangent to the steepest portion of storage modulus vs temperature plots. The value obtained from storage modulus showed a very good agreement with the T_g values obtained from DSC scan. However, T_g obtained from loss modulus plots was higher in all the samples (Table V) but the trends were similar. The presence of more rigid bark filler together with an excellent adhesion between the bark flour and the PVC matrix resulted in restriction of the molecular mobility of the polymer and thereby resulted in an enhancement of T_g . Increase in T_g of polymer matrix using wood flour has also been reported by Rimdusit et al.⁴⁶ The greater the bark flour content, the higher the value of T_g . This is expected because the addition of bark flour in PVC increased the stiffness of the composites, due to dipole-dipole interaction, and thus, increased the T_g .

Morphological characterization

The dispersion of bark flour in the PVC matrix and the interfacial adhesion between the bark flour and PVC matrix were investigated by using scanning electron microscopy (SEM) technique. The SEM technique revealed that the appearance of bark flour pullout in the case of PVC-WF40 (Fig. 7) corresponds to poor adhesion of the two phases. On the other hand, breakage and fibrillation of bark flour were observed (PVC-NWF40), which implies the existence of a substantial degree of adhesion between the two components. It can be seen that bark flour having varying particle sizes exhibited the shape of irregular short fibers in composites. At lower phr of filler, loading bark flour is well dispersed; however, agglomeration of fibers was seen at higher filler loading.

CONCLUSION

From the above work, it is concluded that the flour prepared from the bark of Acacia species and used as a filler in PVC matrix resulted in improving the dimensional stability and mechanical properties (viz., Modulus); however, little decrease in tensile strength is observed, which needs further investigation. Modulus and dynamic properties increased when filler particle size $<50 \mu\text{m}$ was used. These composites can be used as a substitute for wood, which will ultimately control deforestation along with environmental pollution, leading to value-added product, for which much research is sought.

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