Characterization of Highly Filled Wood Flour–PVC Composites: Morphological and Thermal Studies

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ABSTRACT: Composites with polyvinyl chloride (PVC) as major matrix constituent, ethylene vinyl acetate (EVA) as polymeric plasticizer and wood flour (WF) and fly ash (FA) as filler were extruded. Morphology of the samples was studied using scanning electron microscopy (SEM). Morphological study indicated good dispersion of the constituents. Infrared spectroscopy (IR) indicates interaction between EVA and PVC and also between the polymeric matrix and WF. The effect of various constituents on glass transition temperature (T_g) was evaluated using differential scanning calorimetry. Addition of EVA decreased the T_g, whereas T_g was increased due to addition of WF and FA. Study indicated that reduction in T_g on addition of EVA was compensated by increase in T_g due to addition of WF. The contribution of FA to change in T_g was not significant. Resulting composites have T_g close to that of PVC. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 90–96, 2009

Key words: wood-plastic composites; ethylene vinyl acetate; polyvinyl chloride; fly ash; differential scanning calorimetry; infrared spectroscopy; glass transition temperature

INTRODUCTION

Interest in development of wood flour (WF)-thermoplastic composites has been growing in the past few years due to their inherent advantages of high stiffness, strength, low density, and low cost as compared with other inorganic reinforcements like glass fibers, calcium carbonate, talc, etc. The most commonly used thermoplastics in manufacture of wood-plastic composites (WPC) include polyethylene (PE), polypropylene (PP), and PVC. The global market share of PE-based composites is 83%, PVC 9% and PP 7%.[1] PVC has been used as the matrix in the present experimental work. PVC is commonly used in building applications because of its good mechanical properties, chemical and water resistances, low flammability, and low cost. Also, PVC-based wood composites can be cut, sawed, screwed, nailed as standard wood materials using conventional tools.[2] One of the major issues with PVC-WF composites, like other WPCs, is the incompatibility between the hydrophilic WF and hydrophobic plastic matrix. This leads to poor interfacial adhesion, leading to poor dispersion and reduction in mechanical properties. Various compatibilisers have been used for increasing the interfacial adhesion between PVC and WF leading to enhancement in mechanical proper-

ties.[3,4] Ge et al. used a silane coupling agent and studied mechanical and thermal properties along with morphology of PVC-WF composites with WF content varying from 10 to 50 phr. Tensile strength and strain at break was reduced, but there was no appreciable change in the glass transition temperature (Tg) on addition of WF.[5] Djidjelli et al. investigated the effect of addition of WF to PVC on the thermal properties. It was observed that addition of up to 30% WF had an insignificant effect on the T_g.[6] The objective of the present work is to study the effect of addition of both WF and FA as filler in PVC matrix on the thermal properties and morphology of the composites. Composites made are quite cost effective because the FA is a waste product of the thermal power station, and WF is readily available at very low cost. The composites under consideration are designed for structural applications, furniture applications, and as a replacement for commercial plywood.

MATERIAL

PVC was used as the major matrix component and EVA as the minor component. EVA was added as polymeric plasticizer. In addition, it also acts as an impact modifier. Polymeric plasticizers can ease processing without the disadvantages of low-molecular weight plasticizers, which include leaching over a period of time.

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Polyvinyl chloride (PVC)

57 GE R01 grade of suspension PVC manufactured by M/s Reliance India, Ltd. was used.

Ethylene vinyl acetate (EVA)

EVA (Escorene Ultra EVA AD 0428EM1) manufactured byExxonMobil Chemicals (Machelen, Belgium) with 27.5% vinyl acetate by weight was used.

Fly ash (FA)

FA confirming to Class F as per ASTM C 618, with the trade name Pozzoplast, procured from DIRK India, Eklahare, Nasik, India, was used. This FA is obtained from combustion of pulverised bituminous coal. FA contains SiO_2, MgO, Al_2O_3, Fe_2O_3, Na_2O, reactive silica, and chlorides.[7]

Wood flour

Wood is a cellular material. It is a biopolymer that is hygroscopic, viscoelastic, and anisotropic.[8] Wood comprises primarily of four structural components:

1. Cellulose ($\sim$ 45-50% by weight)
2. Hemicellulose ($\sim$ 20-25% by weight)
3. Lignin ($\sim$ 20-30% by weight)
4. Extractives ($\sim$ 5-10% by weight)

Cellulose is a high molecular weight, linear, straight chain homopolymer consisting of chains of with degree of polymerization 5000–10,000. Hemicellulose has lower degree of polymerization (150–200) and is relatively straight or branched. Lignin is a large, amorphous polymer consisting of varying ratios of phenyl propane precursors linked mainly by two or three ether bonds and the rest by C—C bonds. Lignin is often called the cementing agent that binds individual cells together.[9]

The WF used in present work is obtained from Ghana Teak, generically *Tactonna grandis*. WF sieved through 90 mesh and dried for 8 h at 120°C was used for this experimental work.

PROCESSING

PVC and additives were formulated using a high-speed mixer rotating at 1500 rpm. Initially processing aid and lead stabilizer were added. After the mixture reached 80°C, lubricants and dioctyl phthalate (DOP) were added and the rotation was continued till mixture reached 110°C. EVA was added at this stage, if present in formulation. The mixture was cooled. To this, FA and WF were added in the order mentioned and the mixture was mixed thoroughly for 10 min af-ter each addition. The mixture was compounded using a two-roll mill and the hide was reduced in size using a scrap granulator. The granulated material was extruded in the form of sheet the using counter-rotating twin-screw extruder attachment of Brabender Plasticorder, model number AEV 651.

EXPERIMENTAL WORK

Eighteen composites with varying WF, EVA, and FA content were extruded. The numbered code of the samples is based on the parts per hundred (phr) of the constituent i.e phr of WF, FA, and EVA based on PVC. The first number of the code denotes the phr of WF, second number denotes phr of EVA, and the third number denotes the phr of FA, so that 150-10-20 contains 150 phr WF, 10 phr EVA, and 20 phr FA (Table I). For assessing the morphology of the composites, scanning electron microscopy (SEM) of representative composites was carried out using JEOL, model JSM 6360-A Analytical SEM. Infrared spectroscopy (IR) of representative samples was carried out to assess the interaction between the various constituents using a SHIMADZU 470 spectrometer. Thermal behavior of the composites was characterized by differential scanning calorimetry (DSC) using METTLER STAR®SW 8.10. The samples were heated from 30 to 100°C under atmospheric conditions at the rate of 5°C/min.

RESULTS AND DISCUSSION

Scanning electron microscopy

Amongst all the constituents of the composites, FA has the smallest particle size [Fig. 1(a)]. Suspension

TABLE I
Formulations

Sr. no.	Formulation code	Constituents as parts per hundred (phr) of PVC				
		PVC	Additives	WF	EVA	FA
1	PVC	100	11.2	0	0	0
2	PVC + 5 EVA	100	11.2	0	5	0
3	PVC + 10 EVA	100	11.2	0	10	0
4	100-10-0	100	11.2	100	10	0
5	100-10-20	100	11.2	100	10	20
6	100-10-40	100	11.2	100	10	40
8	100-10-60	100	11.2	100	10	60
9	100-5-0	100	11.2	100	5	0
10	100-5-20	100	11.2	100	5	20
11	100-5-40	100	11.2	100	5	40
12	150-10-0	100	11.2	150	10	0
13	150-10-20	100	11.2	150	10	20
14	150-10-40	100	11.2	150	10	40
15	150-10-60	100	11.2	150	10	60
16	150-5-0	100	11.2	150	5	0
17	150-5-20	100	11.2	150	5	20
18	150-5-40	100	11.2	150	5	40
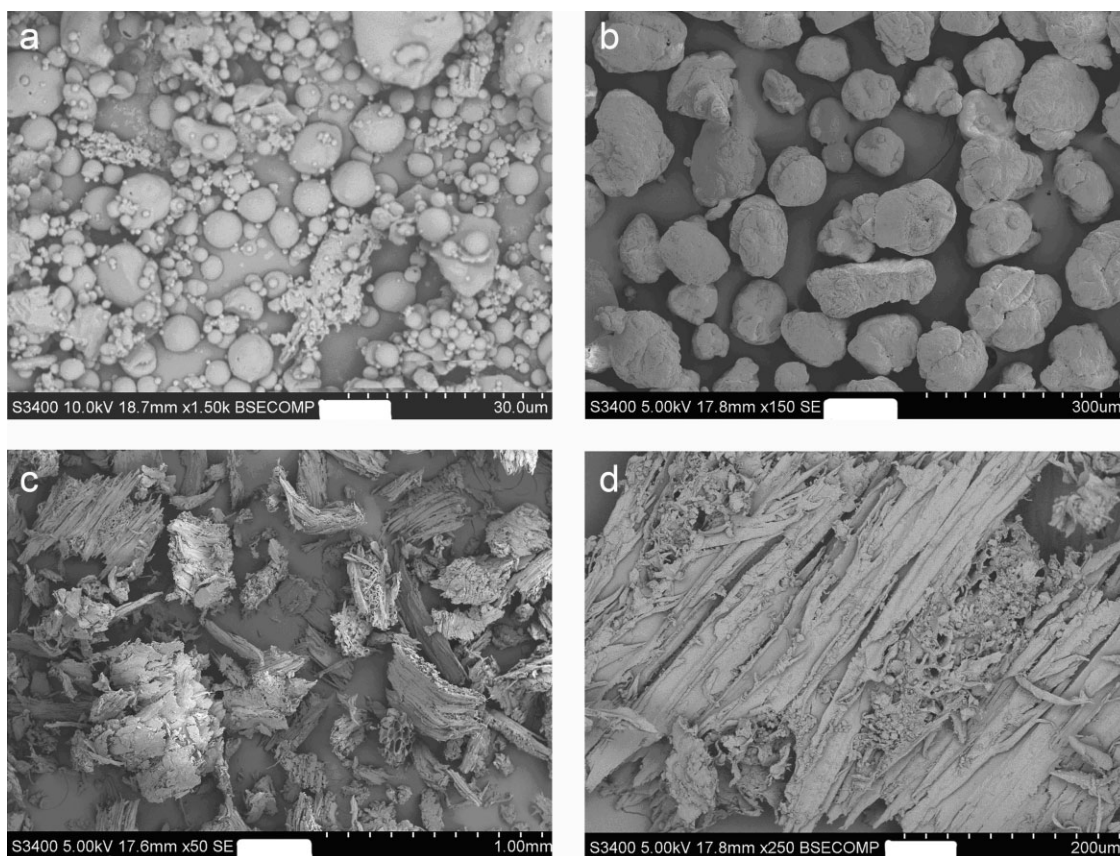
Figure 1 (a) SE micrograph of fly ash, ×1500 magnification; (b) SE micrograph of formulated PVC, ×150 magnification; (c) SE micrograph of wood flour, ×50 magnification; and (d) SE micrograph of wood flour, ×250 magnification.

PVC consists of secondary particles, which are 100 to 150 μm in size. These are made up of primary particles of 0.2 to 1.5 μm in diameter.[10] Size of formulated PVC particles depends on the additives used. In the present experimental work, DOP is one of the constituents, which contribute to swelling of PVC grains [Fig. 1(b)]. During processing, the secondary particles are broken down into primary particles under a specified condition of shear and temperature. WF particles, sieved through 90-mesh size are much larger [Fig. 1(c,d)]. WF is acicular in nature with one dimension larger than the other. During the process of extrusion, the dimension in the direction of extrusion of WF becomes even larger due to orientation and compaction force, giving it a flake like structure. Flake like structure of WF is the principle reason as to why such high loading of WF is possible. Scanning electron micrographs of impact fractured surfaces of PVC + 5 EVA, PVC + 10 EVA, 100-10-0, 100-10-20, 100-10-40, and 150-10-0 were observed under different magnifications. The WF particles have fibrillated nature and larger size, and therefore, the scale of scrutiny is required to be kept large or in other words magnification need to be kept small for understanding the dispersion.

EVA, up to 5 phr remains a dispersed phase in PVC matrix in the form of droplets in the formula-tion PVC + 5 EVA [Fig. 2(a,b)]. Coalescence of droplets is observed on addition of 10 phr EVA to the PVC in the formulation PVC + 10 EVA [Fig. 2(c,d)]. EVA begins to form a coherent phase and on further addition, finally forms a continuous phase.[11] The micrograph for 100-10-0 formulation shows fairly good dispersion [Fig. 2(e,f)]. Also, there is no agglomeration and different phases fairly remain segregated and evenly dispersed. FA is seen as small spheres occupying spaces between the fibrillated WF and the polymeric matrix in the micrograph of 100-10-20 and 100-10-40 [Fig. 2(g–j)].[12] As the wood content goes up, the polymer content reduces to such an extent that even dispersion and binding between the WF and the polymer becomes difficult. Even though extrusion was possible for 150-5-0 and 150-10-0 formulation wherein the WF content is very high, the complete wetting of the WF by polymer is difficult [Fig. 2(k,l)]. Voids are seen in almost all micrographs. FA, being smaller in size than WF, is seen occupying the space in between.

Infrared spectroscopy

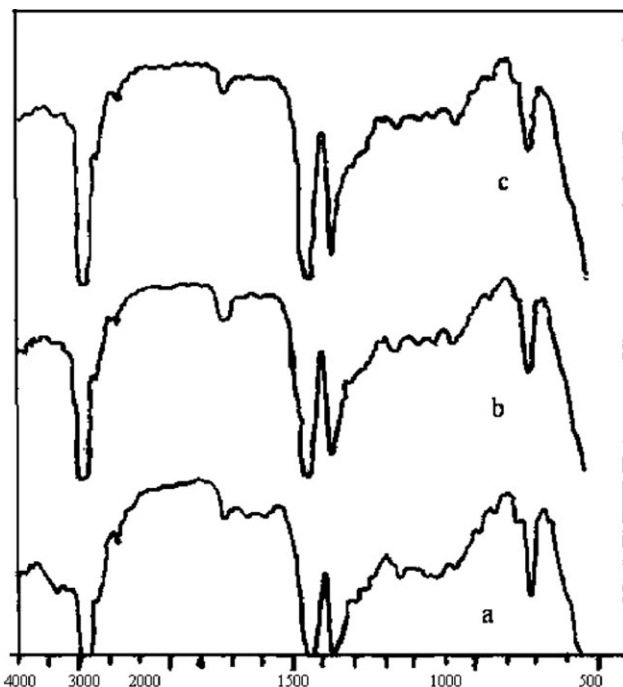In the IR spectra of PVC, PVC + 5 EVA and PVC + 10 EVA, the peak at 1720 cm^{-1} in PVC is due to
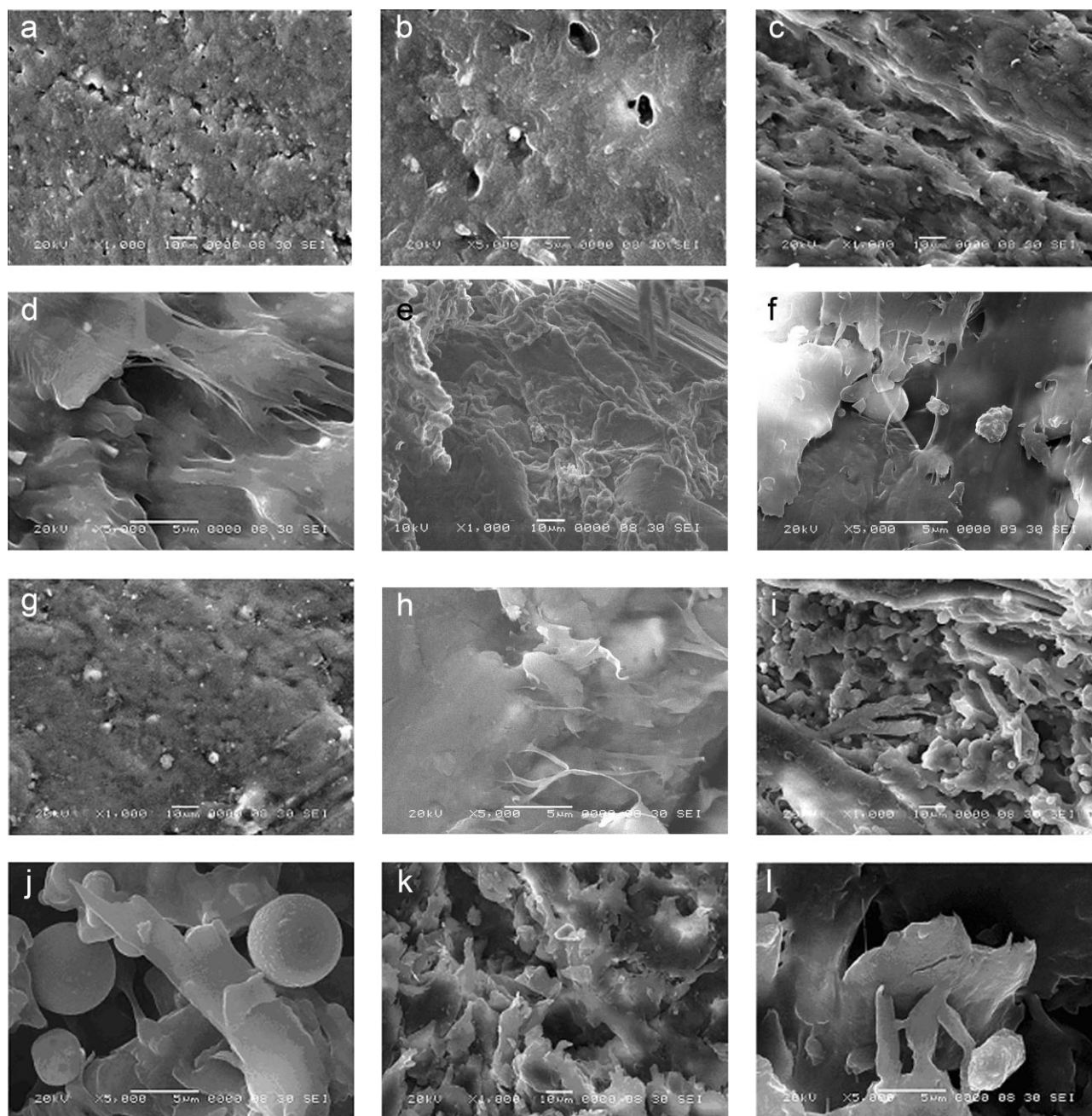
Figure 2 (a) SE micrograph of PVC + 5 EVA at ×1000 magnification; (b) SE micrograph of PVC + 5 EVA at ×5000 magnification; (c) SE micrograph of PVC + 10 EVA at ×1000 magnification; (d) SE micrograph of PVC + 10 EVA at ×5000 magnification; (e) SE micrograph of 100-10-0 at ×1000 magnification; (f) SE micrograph of 100-10-0 at ×5000 magnification; (g) SE micrograph of 100-10-20 at ×1000 magnification; (h) SE micrograph of 100-10-20 at ×5000 magnification; (i) SE micrograph of 100-10-40 at ×1000 magnification; (j) SE micrograph of 100-10-40 at ×5000 magnification; (k) SE micrograph of 150-10-0 at ×1000 magnification; and (l) SE micrograph of 150-10-0 at ×5000 magnification.

carbonyl group present in the plasticizer and the additives used during PVC compounding (Fig. 3). There is a slight shift in the peak at 1720 cm^{-1} in formulated PVC to 1750 cm^{-1} for PVC + 5 EVA and PVC + 10 EVA. The peak also shows broadening. Change in intensity is observed on addition of EVA to formulated PVC. This can be attributed to interaction between the carbonyl group of EVA and

methine hydrogen of PVC. The nature of interaction is the dipole-dipole interaction between the carbonyl oxygen of EVA and the methine hydrogen of PVC.

On addition of WF to PVC + 10 EVA, i.e., for 100-10-0, there is appearance of a peak at 3400 cm^{-1} due to the (—OH) group present in the WF (Fig. 4). Slight shift in the peak at 1750 to 1700 cm^{-1} is observed, indicating interaction between (—CO) group in

Figure 3 IR Spectra of (a) PVC + 5 EVA; (b) PVC + 10 EVA; and (c) PVC.

lignin and methine hydrogen of PVC.[5] Also, increase in intensity and broadening of the peak at 1700 cm^{-1} due to the additional carbonyl groups contributed by the WF is observed.

The difference in the formulation of 100-10-0 and 100-10-20 is the addition of FA in the later formulation (Fig. 5). It is observed that there is an increase in the intensity of the peak at 1700 cm^{-1} in 100-10-20.
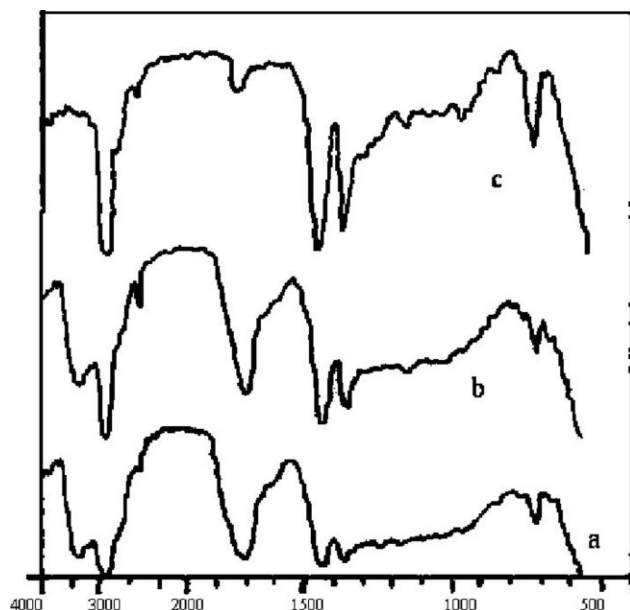
Figure 4 IR spectra of (a) 100-10-0; (b) WF; and (c) PVC + 10 EVA.
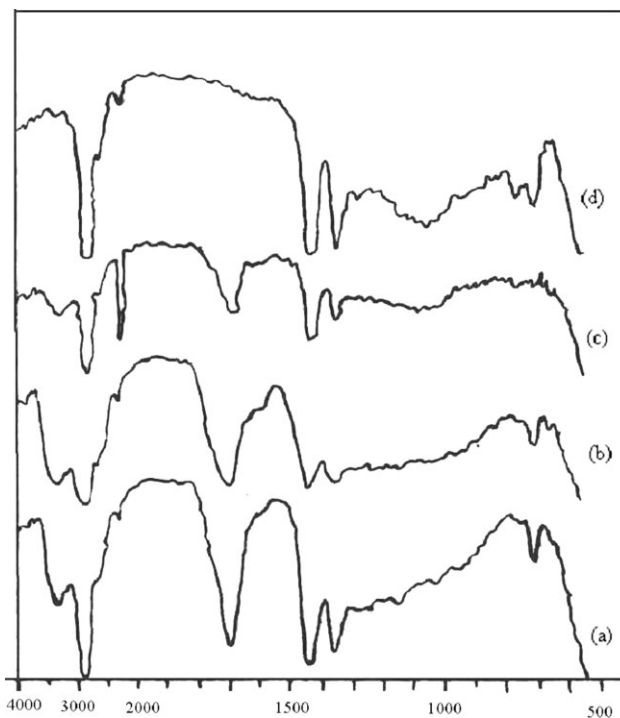
Figure 5 IR spectra of (a) 100-10-10; (b) 100-10-0; (c) FA; and (d) burnt fly ash.

The peaks at 1700 and 3400 cm^{-1} in FA are due to the organic matter present.[10] They contribute in increasing the intensity of peak at 1700 cm^{-1}. The peaks 1700 and 3400 cm^{-1} disappear in the spectra of burnt fly ash. The organic matter in the FA used for the present experimental work was determined by finding out the loss in weight due to heating the FA at 700°C for 2 h. The loss in weight was found to be 0.5095%.

Thermal characterization

The composites were divided into following groups for analyzing their thermal behavior.

- Group A: composites with PVC, PVC, 5 phr EVA
- Group B: composites with PVC, 5 phr EVA, 100 phr, and 150 phr WF
- Group C: composites with PVC, 5 phr EVA, 100 phr WF, and varying FA
- Group D: composites with PVC, 10 phr EVA, 100 phr WF, and varying FA
- Group E: composites with PVC, 5 phr EVA, 150 phr WF, and varying FA
- Group F: composites with PVC, 10% EVA, 150% WF, and varying fly ash

T_g of formulated PVC is 68.8°C. On addition of EVA to PVC, the T_g drops down to 54.0°C (Table II,

TABLE II
Glass Transition Temperature, T_g

Group	sample no.	Sample code	Onset temperature (°C)	Glass Transition temperature (T_g) (°C)	Change in (T_g) over base formulation (°C)
A.	1.	PVC	64.9	67.8	0
	2.	PVC+5 EVA	52.6	54.0	−13.8
B.	1.	PVC+5 EVA	52.6	54.0	0
	2.	100-5-0	67.8	70.6	16.6
	3.	150-5-0	68.6	72.7	18.7
C.	1.	100-5-0	67.8	70.6	0
	2.	100-5-20	67.8	70.9	0.3
	3.	100-5-40	68.8	71.2	0.6
D.	1.	100-10-0	68.2	71.1	0
	2.	100-10-20	69.8	71.9	0.8
	3.	100-10-60	69.3	71.7	0.6
E.	1.	150-5-0	68.6	72.7	0
	2.	150-5-20	67.9	70.2	−2.5
	3.	150-5-40	66.9	71.4	−1.3
F.	1.	150-10-0	67.4	68.5	0
	2.	150-10-20	68.7	70.0	1.5
	3.	150-10-40	66.1	69.8	1.3
	4.	150-10-60	70.0	72.5	4.0

Group A; Fig. 6). EVA forms a miscible blend with PVC in the analyzed temperature range as it shows a single T_g.[13] The considerable drop in T_g is due to low-molecular weight fraction contributed by EVA, which acts as a polymeric plasticiser in the system in consideration.[14]

Lignin in wood is the amorphous matrix in which amorphous hemicellulose and partially crystalline cellulose is embedded. In the absence of compatabilizers, the interaction between the PVC or the EVA with lignin is rather limited. Therefore, rise in T_g observed is not due to interaction between PVC and WF but is primarily due to immobilization of the polymer chains. Addition of the filler takes up free volume. The molecules cannot assume all possible configurational positions. The morphology of the zone around the filler differs from bulk of the polymer. Higher the filler loading more are the number of filler particles associated with the polymer chains and greater is the

immobilization of the polymer chains. This amounts to the stiffening of the polymer chains and hence the rise in the T_g.[15] This results in increase in the T_g by 16.5°C on addition of 100 phr WF to PVC + 5 EVA (i.e., 100-5-0) and that on addition of 150 phr WF (i.e., 150-5-0) is 18.7°C (Table II, Group B; Fig. 7).

Addition of FA to 100 phr WF and 5 phr EVA composites (i.e., 100-5-20), increases the T_g only marginally which indicates the insignificant effect of FA on T_g (Table II, Group C; Fig. 8). Similar results are obtained on addition of FA to 100 phr WF 10 phr EVA composites (i.e., 100-10-20 and 100-10-60) (Table II, Group D; Fig. 9). By and large, addition of FA to 150 phr WF and 5 phr and 10 phr EVA composites (i.e., 150-10-20, 150-10-40, 150-10-60, 150-5-20, and 150-5-40) has a similar effect (Table II, Groups E and F; Figs. 10 and 11). Overall, FA has insignificant effect on the T_g.
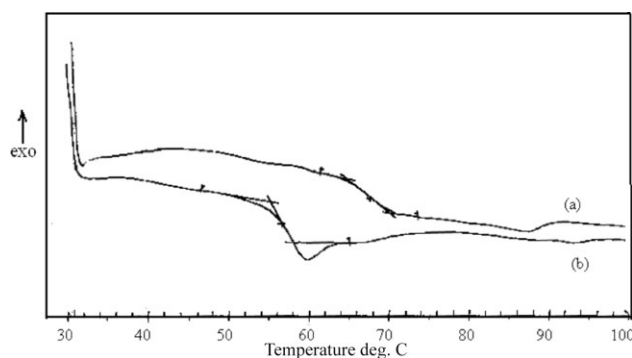

Figure 6 DSC thermogram for Group A composites (a) PVC and (b) PVC + 5 EVA.
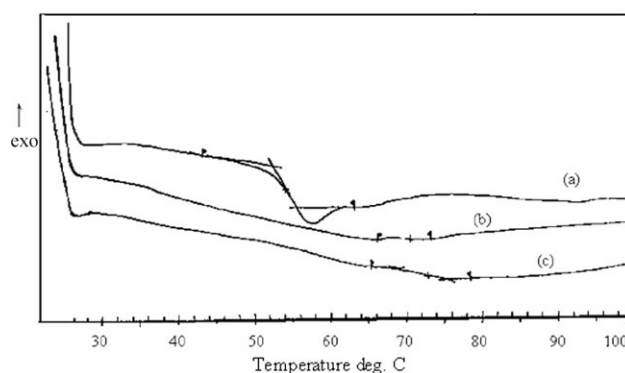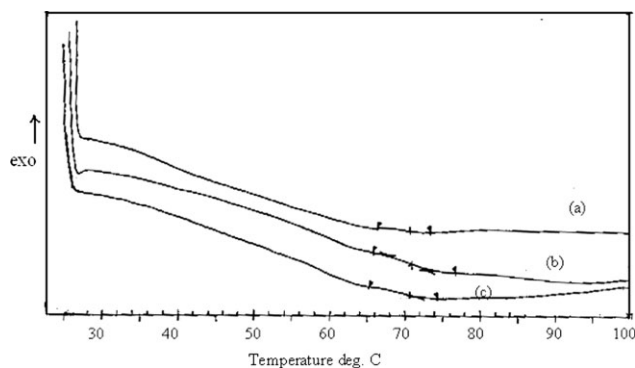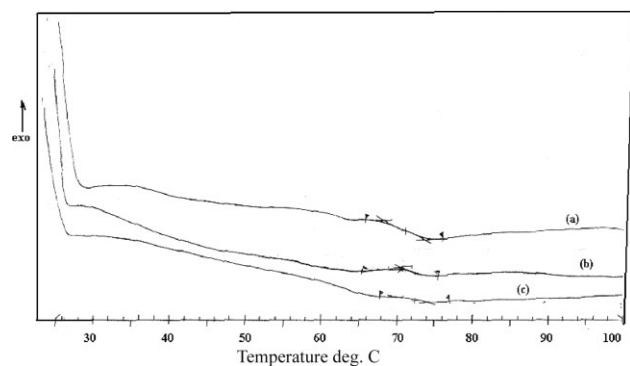

Figure 7 DSC thermogram for Group B composite (a) PVC + 5 EVA, (b) 100-5-0, and (c) 150-5-0.
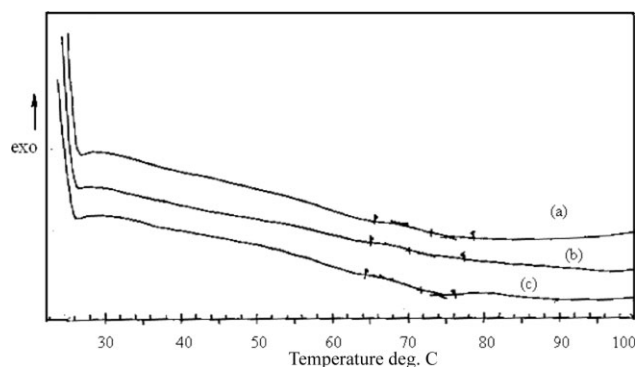
Figure 8 DSC thermogram for Group C composites (a) 100-5-0, (b) 100-5-20, and (c) 100-5-40.
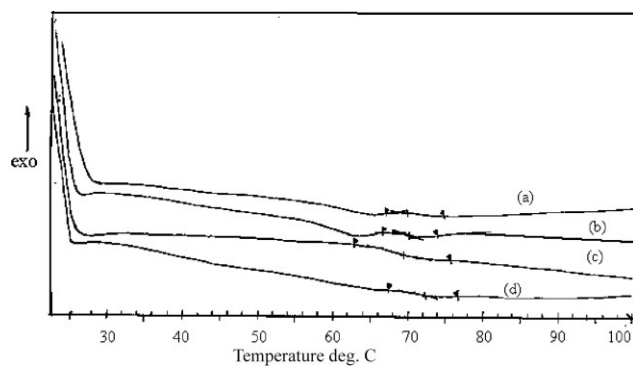

Figure 9 DSC thermogram for Group D composites (a) 100-10-0, (b) 100-10-20, and (c) 100-10-60.

CONCLUSIONS

Scanning electron micrographs show fairly good dispersion of the constituents in final composite. Infrared spectroscopy indicates interaction between PVC and EVA. Interaction between the polymeric matrix and WF is also seen. Thermal analysis shows initial decrease in the T_g on addition of EVA indicating its plasticizing effect. Lowering and single value of T_g in the analyzed temperature region indicates the miscibility of PVC and EVA. Addition of WF to this

Figure 10 DSC thermogram for Group E composites (a) 150-5-0, (b) 150-5-20, and (c) 150-5-40.

Figure 11 DSC thermogram for Group F composites (a) 150-10-0, (b) 150-10-20, (c) 150-10-40, and (d) 150-10-60.

matrix increases the T_g substantially, indicating the stiffening effect of the filler on the composite. Contribution of FA in enhancing the T_g is not significant.

EVA is primarily used for its plasticizing effect and ease of processing. The drop in T_g due to addition of EVA is compensated on addition of WF. Hence, the final composites have T_g very close to that of PVC and thereby similar service temperature.

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