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Thermal Behavior of Composites Based on Poly(vinyl alcohol) and Sugar Cane Bagasse

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Summary: Poly(vinyl alcohol) (PVA) and sugar cane bagasse (SCB) mixtures have been formulated as aimed at the production of hydro-mulching composites and melt processed biobased composite items. Glycerol and urea have been proposed as suitable plasticizers and eventually, in the case of urea, for the realization also of slow release fertilizing hydro-mulching. The investigation of thermal stability of raw components and relevant mixture is an important parameter to be assessed in view of processing and ultimate applications. PVA/SCB composites appeared suitable for melt processing up to 200 °C. The urea containing PVA/SCB composites while resulted particularly suited for hydro-mulching applications did not appear processable from the melt, due to urea thermal instability.

Keywords: bagasse; composites; poly(vinyl alcohol); renewable resources; thermal properties

Introduction

The waste management problems associated with petroleum based synthetic plastics has attracted the attention of researchers and municipal authorities on materials from renewable resources that may be essentially turned out to be eco-compatible.[1]

In Europe, the European Commission (EC) has issued directives dealing with the problems of waste disposal and particularly from waste packaging which represents the largest share of plastic consumption.[2-4] In this connection the EC Directive “On the Landfill of Waste” issued in 1999 is dictating a progressive reduction of the amount of the organic fraction in the municipal solid waste to a level of 75% in year 2006, 50% in year 2009 and 35% in year 2016 of the total organic fraction present in the municipal solid waste in year 1995.[5] This directive is going to be integrated with the Biowaste Directive that is expected to be issue by EC in 2004.

Degradable-plastic composites are emerging materials that offer benefits to the environment resulting in minimization of waste that would be otherwise disposed in landfills. Thus environmentally compatible materials derived from renewable sources can serve in some

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applications as convenient substitutes of petroleum-based polymers. The use of natural fibres as fillers and reinforcement materials in plastic composites is of particular interest to help designing bio-based polymeric materials meant to be converted to eco-compatible plastic articles.[6-10]

Single-use plastic materials, with particular reference to the packaging, agriculture and consumer product segments such as cups, containers, cutlery, mulching films, transplanting pots, etc., have been identified as suitable items to be replaced by bio-based biodegradable materials leading to a better ecological compliance.[11, 12]

As a part of our continuing research interest in the preparation and evaluation of environmentally degradable polymers for various applications in agricultural practices, with specific reference to the *in situ* formulation of self-fertilizing mulching and solarizing films, we developed degradable films based on PVA and ligno-cellulosic fillers as attainable by casting or directly spraying water suspensions of the polymeric components.[13-16] The presence of sugar cane bagasse (SCB) in PVA based water suspensions showed to enhance PVA soil structuring effect and time of duration of the treatment applied on the soil.[17] Moreover the presence of ligno-cellulosic fillers in composites bound to degrade directly in situ after life service have the added value effect of releasing the ligno-celluloscis in the soil, which will convert to humic substances, with positive agronomic effects. PVA/ligno-cellulosic composites production by compression moulding and injection moulding are also under development in our laboratories.[18, 19] Mechanical properties of the PVA/ligno-cellulosics composites resulted to be dependent of the polymer/fiber ratio and type and amount of plasticizers introduced in the formulations [15, 19].

In the present study glycerol and urea have been proposed as suitable plasticizers for PVA/SCB composites. Urea was chosen as a component suited to provide agricultural items susceptible of acting as slow release fertilizing systems. The investigation of thermal stability by thermal gravimetric analysis (TGA) of raw components and relevant mixtures is an important parameter to define range of applications and processability of PVA/SCB composite materials.

The assessment of the effect of each single component appeared to provide useful guidance in the selection of formulation compositions and in understanding the effect of the interactions of the components in the various composite systems. SCB thermal behaviour and its effect on PVA based composites, also in the presence of glycerol and urea, has been investigated by differential scanning calorimetry (DSC).

Experimental

Materials. Poly (vinyl alcohol) Mowiol 08/88 (Mw 67 kD, hydrolysis degree 88%) was purchased from Erkol, Spain, and used as received. Sugar cane bagasse (SCB) fibres from Copersucar (Brazil) were obtained by milling and sieving through a 70 mesh ASTM sieve (# < 0.212 mm). SCB utilized consisted of: crude fibres 42.6%, cellulose 29,2%, lignin 10.5%, crude protein 9.1%, fat 2.6%, ash 6.0%.

Glycerol and urea were reagent grade and were purchased respectively from Baker and Carlo Erba. They were used as received.

Sample Preparation. Composites laminates based on PVA and SCB were prepared by weighing the appropriate amount of a 10 % by weight PVA water solution into a 100 ml conical flask, then adding SCB. PVA/SCB composites were prepared from 10% to 50% content by weight of SCB. The PVA/SCB 1/1 by weight composite was selected to investigate the effect of glycerol and urea addition on thermal properties of the final composites. Thus keeping constant PVA/SCB ratio, 6 to 20 % by weight of respectively glycerol and urea were added to the PVA water solution in water under stirring, before the addition of SCB (Table 1). After stirring for 1h at 80 °C, the mixtures were cast in teflonated dishes.

Table 1. Composition of hybrid composite films based on PVA/SCB

Sample	PVA (wt-%)	SCB (wt-%)	Urea (wt-%)	Glycerol (wt-%)
PSCB50	50	50	—	—
PSCBG6	47	47	—	6
PSCBG10	45	45	—	10
PBSCG14	43	43	—	14
PSCBG16	42	42	—	16
PBSCG20	40	40	—	20
PSCBU6	47	47	6	—
PSCBU10	45	45	10	—
PBSCU14	43	43	14	—
PSCBU16	42	42	16	—
PBSCU20	40	40	20	—

Thermal Gravimetric Analysis (TGA). A Mettler TA4000 System consisting of TG50 furnace, M3 microbalance and TA72 GraphWare was used for thermogravimetric measurements. Samples (about 10 mg) were heated from 25 to 600 °C at a 10 °C/min scanning rate, under nitrogen atmosphere (flow rate about 200 ml/min).

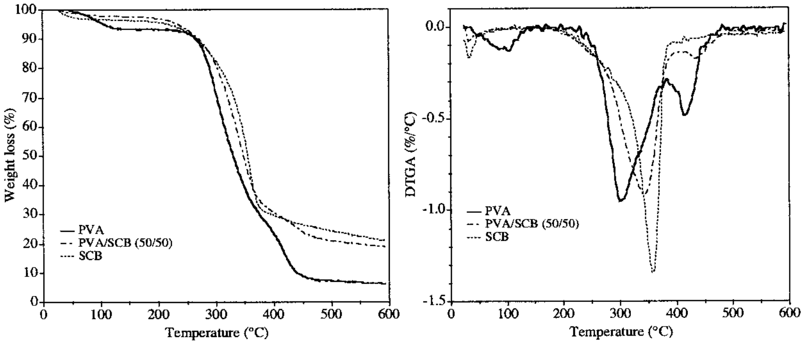
Differential Scanning Calorimetry (DSC). DSC measurements were carried out on a Mettler TA4000 system connected to a TA72 Graphware,under nitrogen flow (ca. 100 ml/min.). About 15 mg samples were weighed in hermetic aluminium pans (40 µl capacity). Composites and single component samples were heated from 0 °C to 130 °C (10 °C/min), cooled to 0 °C (100 °C/min), and heated again from 0 °C to 220 °C (10 °C/min).

Results and Discussion

After moisture loss, thermo-decomposition of PVA and its composites mostly occurred in two steps,while SCB in only one. Figures 1a and 1b show respectively integral and derivative TGA traces of PVA, SCB and respective 50 wt-% composite. Table 2 presents the values of moisture amount, temperature at which 1 wt-% neat weight loss occurs (T_l) and that of onset thermo-decomposition (T_{on}) and residue evaluated at 600 °C. T_l and T_{on} are two way to define decomposition temperature.[20] T_l is related with the early stage of thermal decomposition. This temperature is fundamental when defining melt processing one. T_{on} is defined being the temperature at the crossover of tangents drawn on both sides of the first decomposition step will be higher than T_l and depends of the rate of decomposition. T_l and T_{on} values of PVA/SCB composites were placed between those of PVA (244 °C and 265 °C, respectively) and SCB (154 °C and 230 °C, respectively) decreasing with increasing of the content of less stable SCB component. Besides, PVA/SCB composites leave more char residue than PVA matrix itself. Considering that there is a direct relationship between char residue and oxygen index (index of the flame resistance)[21], it is highlighted that PVA/SCB composites can be less flammable than PVA itself.

All materials presented a moisture level of about 5 wt-% due to the characteristic hygroscopicity of both composites components.

Figure 2 (a) shows DSC traces of PVA based composites from the second heating scanning as a function of SCB loading. As comparison reference, the glass transition temperatures (T_g) of PVA (59 °C) and SCB (118 °C) and PVA (191°C) melting peak were delineated in the figure.



(a) (b)

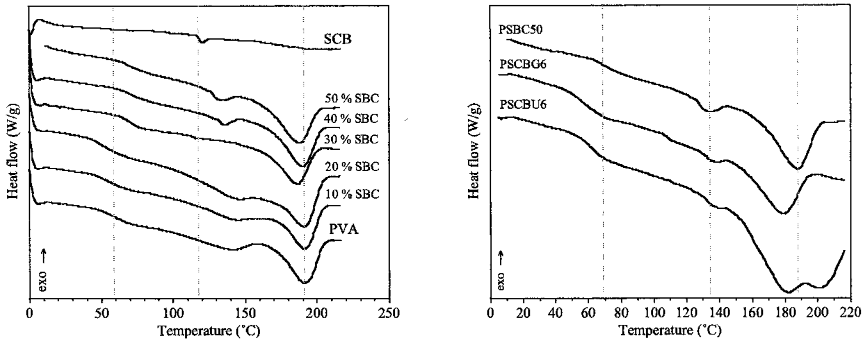
Figure 1. TGA (a) and DTGA (b) traces of PVA, SCB and respective 50 wt-% composite.

Table 2. Thermogravimetric data from PVA/SCB composites.[a]

Sample PVA/SCB	Moisture (wt-%)	T_1 (°C)	T_{on} (°C)	Residue (wt-%)
100/0	6	244	265	6
90/10	4	215	257	10
70/30	5	200	260	13
50/50	4	182	236	16
0/100	5	154	230	20

[a] T_1 = temperature at which 1 wt-% neat weight loss occurs. T_{on} = onset decomposition temperature. Residue at 600 °C.

PVA displays two endotherms with peak temperatures at 141 °C and 191 °C, respectively. Probably, the former broad endotherm is due to a residual moisture remained after the first heating until 130°C. The peak temperature of this transition increases slightly in composites loaded up to 20 wt-% of SCB and disappears for composites containing more than 30 wt-% of SCB. This slight increase can be attributed to a decrease on diffusion rate of moisture with the addition of SCB. The second endotherm is related to the melting transition of PVA in composites and basically the peak temperatures (T_m) of this transition are not affected by the presence of SCB. However, a small decrease of T_m was observed for composites loaded with 30 wt-% of SCB.



(a) (b)

Figure 2. Second heating DSC traces of (a) PVA/SCB composites and (b) 6 wt-% plasticized composites.

The addition of SCB up to a load of 20 wt-% does not influence significantly the T_g of PVA. However, for higher loads of SCB up to 50 wt-%, T_g of PVA increased by about 10 °C. This increasing may be due to the reinforcing property of SCB in concurrence to the less residual moisture in the composite after the first heating up to 130 °C. PVA/SCB interactions . The reinforcing property of SCB was verified in a DMTA study of these composites.[22]

DSC trace of PVA/SCB composite containing 30 wt-% of SCB indicates a second small change in the heat capacity at ca. 115 °C that probably corresponds to T_g of SCB.[23, 24] On the other hand, is not easy the assignment of the transitions at about 134 °C for PVA composites loaded with more than 40 wt-% of SCB. By supposing that this transition be related to T_g of SCB, the increasing of about 20 °C from single SCB could be explained by structural changes. Another hypothesis is that this transition corresponds to a melting of imperfect PVA crystals formed at higher amount of SCB.

Plasticized composites were prepared by keeping constant the PVA/SCB 50/50 ratio (PSCB50) and adding from 6 to 20 wt-% of respectively glycerol and urea as reported in Table1. In Figure 2 (b) the PVA/SCB (1:1) composites plasticized with 6 wt-% of either glycerol or urea, as in PSCBG6 and PSCBU6, exemplify the effect of plasticizer addition into these composites. The resultant thermal parameters are reported in Table 3. Addition of plasticizer in PVA/SCB (1:1) composite decreased both T_g and T_m of PVA as expected principally in the case of glycerol [25]. T_g's of plasticized PVA/SCB composites decreased by 50 °C for 20 wt-% of glycerol and by 30 °C for 20 wt-% of urea.

Table 3. Thermal parameters of PVA/SCB composites plasticized with glycerol or urea

Sample	$T_{g\,PVA}$ (°C)	$T_{g\,SCB}$ (°C)	$T_{m\,PVA}$ (°C)	Sample	$T_{g\,PVA}$ (°C)	$T_{g\,SCB}$ (°C)
PSCB50	68	131	188			
PSCBG6	55	133	178	PSCBU6	62	133
PSCBG10	45	136	172	PSCBU10	53	134
PSCBG14	30	134	165	PSCBU14	44	134
PSCBG16	20	134	160	PSCBU16	38	134
PSCBG20	17	134	157	PSCBU20	38	134

By calculating the T_g's of miscible PVA/glycerol blends from Fox equation (eq. 1)[26] and comparing with experimental results of plasticized PVA/SCB composites can be attained an idea of the SCB filler contribution. The T_g's of PVA cast film and glycerol are 59 °C and -77 °C respectively.

$$\frac{1}{T_{gB}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad \text{(eq. 1)}$$

Where w_1 and w_2 represents the mass fractions of the components and T_{gB}, T_{g1} and T_{g2} are the T_g's of the blend, component 1, and component 2, respectively in Kelvin

Figure 3 reports the calculated T_g's of PVA/glycerol blends and experimental T_g's results of plasticized PVA/SCB composites as a function of glycerol concentration. As can be observed up to 10 wt-% of glycerol the T_g's of plasticized composites are ca. 10 °C higher than that predict by Fox equation for binary blends PVA/glycerol. For superior glycerol amount, experimental T_g's basically overlap the calculated one. SCB maintain its reinforcing property in the plasticized PVA-50 wt-%SCB composite up to 10 wt-% of glycerol.

The transition at ca. 134 °C did not change independently of the type or amount of plasticizer, thus substantiating the above hypothesis that this transition is corresponding to T_g of SCB.

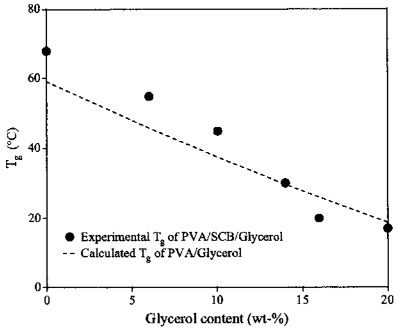


Figure 3. Glass transition temperature-composition relationship of PVA/SCB composites plasticized with glycerol.

It was observed that PVA/SCB composites with more than 14 wt-% of plasticizer (PSCBG16, PSCBG20, PSCBU16, PSCBU20) exuded liquid glycerol and crystals of urea with aging. Moreover in both cases (glycerol and urea) additional increasing of the additive did not contribute significantly to the change of the PVA glass phase.

Melting temperatures (T_m) of PVA in PVA/SCB/glycerol composites decreased linearly with the increase of glycerol. Thus the T_m expected lowering, as consequence of glycerol addition, was not influenced by the presence of SCB filler. This aspect is particularly important in view of melt processing trials on PVA/SCB mixtures.

Conclusions

Thermal stability of PVA expressed by the onset temperature (T_{on}) was appreciably higher than that of bagasse. Composites T_{on}'s values were found between that of each single component

The lowering of the melting temperature observed upon the addition of glycerol in PVA/SCB mixtures constitutes an important effect in view of thermal processing of PVA/lignocellulosic formulations. Plasticized (1:1) PVA/SCB composites behave as reinforced material for formulations containing up to 10 wt-% of glycerol. Both glycerol and urea resulted effective in lowering T_g of PVA in composites with SCB. Although urea is a good plasticizer for PVA and a fertilizing agent, its degradation at the melt processing temperature confines the use of processing of relevant mixtures by casting or spraying from aqueous formulations. This aspect is important for the planned applications of the studied mixtures as liquid mulch and soil structuring agent

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