

# Hybrid Composite Based on Poly(vinyl alcohol) and Fillers from Renewable Resources

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**ABSTRACT:** Hybrid composite laminates consisting of polyvinyl alcohol (PVA) as continuous phase (33% by weight) and lignocellulosic fillers, derived from sugarcane bagasse, apple and orange waste (22% by weight) were molded in a carver press in the presence of water and glycerol such as plasticizers agents. Corn starch was introduced as a biodegradation promoter and gluing component of the natural filler and synthetic polymeric matrix in the composite (22% by weight). The prepared laminates were characterized for their mechanical properties and degradative behavior in simulated soil burial experiments. The fibers type and content in composite impacted mechanical properties. Materials based on PVA and starch

with apple wastes and sugarcane bagasse fillers were much harder (Young's Modulus respectively, 57, 171 MPa) than materials prepared with orange wastes (17 MPa). Respirometric test revealed that soil microbes preferentially used natural polymers and low molecular weight additive as a carbon source compared to biodegradable synthetic polymer. The presence of PVA in formulations had no negative effect on the degradation of lignocellulosic fibers. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1684–1691, 2008

**Key words:** polyvinyl alcohol; lignocellulosic fillers; composite; biodegradable; compression molding

## INTRODUCTION

Environmentally compatible products are being developed as an alternative to petroleum-based synthetic materials. Particularly, much importance has been placed to seek suitable alternatives for conventional plastics used in the manufacturing of single-use consumer products, and in the market segments of containers for liquid and solids and packaging that by themselves adsorb between 30 and 40% of the overall plastic consumption.<sup>1</sup> This poses genuine environmental concerns, as most of the quoted items are based on polymeric materials recalcitrant to environmental degradation once their service life is over.<sup>2</sup>

It is expected that in the near future biodegradable polymers will replace synthetic polymers, at least in some specific applications, where a short life of the

product will be much desirable. Natural polymers are considered suitable to replace synthetic ones in some specific applications where a long span life is not required even if natural polymers may be penalized by an impair cost/performance balance.<sup>3</sup>

Materials such as renewable crops, agricultural waste and/or by-products are a good source of natural polymeric materials that are comparatively less expensive.<sup>4</sup> Among them there are considerable quantities of agro-based fibers available on a worldwide basis for a variety of applications.<sup>5</sup> The poor dimensional stability and lack of thermoplasticity of lignocellulosic fibers have limited the use of these materials to produce single use products. For these reasons fibrous materials have been mixed with thermoplastic matrices to provide hybrid composite containing various percentages of natural fibers.<sup>6</sup>

In this regard, polyvinyl alcohol (PVA), a hydrolysis product of polyvinyl acetate, is well suited for blending with natural polymers since it is a highly polar synthetic polymer and is also considered biodegradable.<sup>7</sup> The PVA molded items have good physical properties such as Tensile Strength and Elongation at Break. For these reasons PVA has been extensively used to improve mechanical properties in blends with natural polymers.<sup>8–12</sup> Thus PVA has been used in solution form to produce films with thermoplastic starch by casting and calendaring for several uses such as agricultural mulch films and

Names are necessary to report factually on available data; however the USDA neither guarantees nor warrants the standards of the product, and the use of the name USDA implies no approval of the product to the exclusion of others that may also be suitable.

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**TABLE I**  
**Composition of Lignocellulosic Fillers Utilized in the Formulation of Composite Mixtures**

Fillers <sup>a</sup>	Protein %	Crude fat %	Filler %	Ash %	Cell/Hem/Pect %	Lignin %	Moisture %
SC	4.22	1.97	31.70	11.41	34.64	10.56	5.54
OR	12.88	6.60	14.74	11.30	39.84	4.76	9.88
AP	4.66	11.48	27.33	1.27	26.80	21.06	7.40

<sup>a</sup> SC = Sugar cane bagasse, OR = Orange by-products, AP = Apple byproducts Cell/Hem/Pect = Cellulose, hemicellulose, pectin.

water-soluble laundry bags.<sup>13–16</sup> Cast films made from PVA and cellulose showed good miscibility due to their mutual ability to form intramolecular hydrogen bonds between hydroxyl groups.<sup>17</sup> Cast films of PVA-Pectin from water solution have also been reported.<sup>18</sup> PVA and bioglass composite have been prepared and investigated for biomedical applications.<sup>19</sup>

PVA is water soluble in different ranges of temperature depending upon composition. It displays a thermoplastic behavior in the melt even though with moderate thermostability, and tends to undergo a fairly fast biodegradation in aqueous medium.<sup>20</sup> By virtue of these characteristics PVA is indeed a well suited polymeric material for the formulation of hybrid composites as attainable by melt processing, compression molding or casting from aqueous dispersions.<sup>21–23</sup>

Previously, we have reported the preparation of composite films containing PVA and lignocellulosic fibers derived from sugarcane, apple and orange waste.<sup>24</sup> Cast films prepared from aqueous suspension showed interesting properties particularly in the case of films and laminates produced by casting mixtures based on PVA and orange waste.

Solution processing is generally considered uneconomical due to the high processing cost and low efficiency in comparison to thermoplastic processing.

This paper describes our efforts in processing of melt PVA and lignocellulosic fibers for the fabrication of hybrid composite items susceptible to undergo controlled environmental biodegradation. The effect of the starting mixture composition on the compression mold-ability and on mechanical and degradative properties of the molded items was investigated.

## EXPERIMENTAL

### Materials

Polyvinyl alcohol was purchased from Air Products and Chemicals, Allentown, PA. Airvol 425 was 95.5–96.5% hydrolyzed with an average molecular weight of 100,000–146,000. Glycerol and urea were purchased from Fisher Chemicals, and Sigma Chemical Company, St. Luis, MO, respectively. Unmodified

commercial-grade corn/starch (Buffalo 3401) was obtained from CPC International, Argo, IL, with ~30% amylose and 70% amylopectin. Cellulosic materials were from three different sources orange (OR) and apple (AP) were the remains of fruit residue after juice extraction supplied by the Sunflo Cit-Russ Limited, Lahore, Pakistan and Taneer's Orchard, Peers, Illinois, USA, respectively; sugarcane bagasse (SC) was supplied by US Sugar Corp., Florida. All cellulosic materials were milled, sieved through a 12xx Swiss Silk to obtain 0.153-mm size particles, and analyzed to determine their composition and moisture properties (Table I).

The soil inoculum for biodegradation studies was Topsoil from Prairie Garden, Bluestem Products, Cedar Rapids, IA, with 50% moisture content, and was further stabilized and matured for more than 3 months in the laboratory.

### Preparation of composites by compression molding

Weighted amount of plasticizer was dissolved in water, then the desired amount of PVA, organic filler and starch was added to the resulting solution. The different components were premixed in a kitchen Aid mixer and the resulting mixture was slowly introduced in a FA/R-2 Brabender mixer (South Hackensack, NJ), operating at an oil bath temperature of 185°C. The mixing was carried on at low speed (speed 1) for 15 min. The mixed samples were kept in the mold and then pressed with a model 2518 Carver Laboratory Press at 180°C. Samples were kept in the mold for 15 min then pressed at 14 ton for 20 min before cooling down at room temperature before they were retrieved. Compositions of the starting PVA/organic filler mixtures used for the composites production are reported in Table II.

### SEM analysis

For scanning electron microscopy (SEM), samples were mounted on aluminum stubs with graphite filled tape, vacuum coated with gold-palladium and examined under the scanning electron microscope (JEOL JSM 6400V, JEOL, Peabody, MA). Fractures surfaces were prepared under liquid nitrogen.

**TABLE II**  
Composition of the Mixtures Used to Prepare the Composites by Compression Moulding

Sample	PVA (wt-p)	Fillers		Starch (wt-p)	Glycerol (wt-p)	Urea (wt-p)	H <sub>2</sub> O (wt-p)
		Type	(wt-p)				
PStG	150	–	–	100	100	–	100
PORG	150	OR	100	–	100	–	200
PStOR	150	OR	100	100	100	–	300
PStAP	150	AP	100	100	100	–	300
PStSC	150	SC	100	100	100	–	300
PStORU	150	OR	100	100	100	100	200

wt-p = weight parts.

### Mechanical testing

Elongation at break (El), Ultimate tensile strength (UTS), and Young's modulus (YM) for each film were measured using an Instron Universal Testing System (Instron, Canton, MA). The gauge length was 25 mm, the grip distance was 45 mm and the cross-head speed of the Instron was 10 mm/min. Data were collected at a rate of 20 pt/s. At least five specimens for each sample were tested and data were averaged.

Impact strength tests were performed on compression molded disks with 6.4-mm diameter and 3.4-mm thickness by a Dynatup Impact tester (drop weight) (Instron, Canton, MA) operating at 3.0 m/s speed and 53 J Impact Energy. At least five specimens for each sample were tested and data were averaged.

### Respirometric test

About 500 mg of a composite sample containing PVA, OR, starch and glycerol (PORSt), and the corresponding amounts of PVA (165 mg) and fillers composed by OR, starch and glycerol (ORSt) (335 mg) were dried up to constant weight and ground. The resulting powders were mixed with 25 g of compost soil in the sample chamber of a closed circuit Micro-Oximax respirometer system (Columbus Instruments, Columbus, OH) equipped with expansion interface, condenser and a water bath. Samples chambers were placed in the water bath thermostated at 25°C and connected to the Micro-Oximax respirometer. The total CO<sub>2</sub> evolution was recorded every 6 h. Experiments were carried out over a period of 21 days.

### Simulated composting of compression molded specimens

Sixteen dog bones shaped ASTM D-638 type IV tensile specimens, cut stamped out of a composite

based on PVA, OR starch, and glycerol (PORSt) and a composite-based PVA, OR, starch, glycerol and urea (PORStU) were buried in two rectangular pots (35 × 19 cm<sup>2</sup>, 6-cm height) containing 1750 g of soil compost having 50% moisture content. The pots were stored, in the dark, in a Percival growth chamber thermostated at 25°C without light exposure. Soil was humidified every day to maintain 50% moisture content. Four specimens of each sample were recovered after 1 and 2 months of burying. Weight loss and dimensional changes measurements as well as mechanical tests were performed on starting and buried samples.

## RESULTS AND DISCUSSION

### Processing and mechanical properties

Previously we have reported composites films based on PVA and SC, AP, and OR prepared by casting aqueous suspension.<sup>24</sup> Particularly films based on PVA and OR showed to be homogeneous, flexible and more cohesive than composites based on PVA and SC or AP.<sup>25</sup> Thus OR was selected for the first attempts to produce composites by compression molding.

A mixture composed of PVA, OR, and glycerol in the proportion 150/100/100 was previously mixed in a kitchen mixer and subsequently in a Brabender mixer, heated by oil bath, at 185°C. The mixture didn't appear perfectly amalgamated after mixing, in the kitchen mixer. When the mixture was introduced in the Brabender mixer, fibers smelled for burning and by compression molding only a dry, burned, extremely hard, and brittle aggregate was obtained. The high molecular weight of PVA required a too high processing temperature to melt; that as estimated by DSC was around 210°C (data not shown). High processing temperatures induce decomposition both on the fibers and on PVA itself.

For processing of mixtures of natural fibers or starch, as well as PVA, water is often added in addition to glycerol<sup>26</sup> or similar plasticizer (sorbitol, sucrose).<sup>27</sup> The plasticizing role of the water lowers the melting temperature of the blend and the viscosity, and allows a more thorough mixing of the blend under the processing conditions as a result of the interaction of the hydroxyl groups of synthetic polymers with the water.<sup>28</sup> Lowering of the processing temperature was beneficial because lower temperatures would avoid degradation of natural fibers and starch, and save energy. On the other hand water's action as a blowing agent created many voids in the composite material, that are supposed to impact its mechanical properties.<sup>29</sup>

The introduction of water in the formulations produced a more amalgamated and cohesive mixture

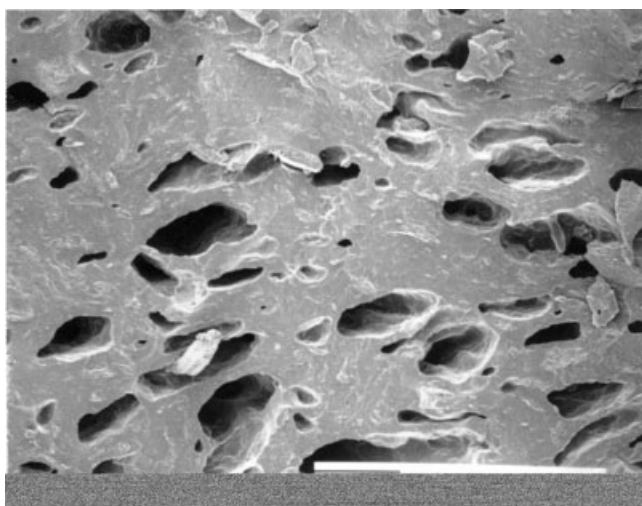


Figure 1 SEM micrograph ( $\times 150$ ) of PStOR fracture.

also in the kitchen mixer. When the mixture was introduced in the Brabender mixer it melted easily in about 10–15 min. No smell of burn was produced and the resulting paste was cohesive and homogeneous. By compression molding a uniform, flexible hybrid composite laminate was produced. Thus all the laminates were prepared from mixture previously amalgamated in water presence. Composition of the mixture used for the production of the hybrid composites is reported in Table II.

SEM analysis of fractures of these hybrid composites evidenced the presence of voids as a result of water evaporation during processing (Fig. 1). Irregularity of these voids might be a result of temperature fluctuations or entrapped air. Interestingly, these imperfections improved the flexibility of the molded material and stimulated the degradation as observed in the soil burial test of molded specimens.

When processed by compression molding a mixture of 150 parts of PVA and 100 parts of starch produced a hard and fragile composite laminate. Introduction of glycerol, PVA/Starch/Glycerol 150/100/100 (PStG), increased flexibility but leaching of glycerol with ageing was very high. When starch was

TABLE III  
Mechanical Properties of Composites Based on PVA and Lignocellulosic Fillers

Sample	EI (%)	StDv	UTS (MPa)	StDv	YM (MPa)	StDv
PStG	67	10	4.8	0.5	17.8	0.6
PORG	68	5	3.7	0.4	16.3	1.1
PStOR	56	2	3.4	0.1	15.3	1.1
PStAP	61	10	9.3	0.4	57	6.1
PStSC	7	1	8.1	1.8	171	31
PStORU	148	22	1.2	0.1	2.1	0.3

StDv = Standard Deviation, EI = Elongation at Break, UTS = Ultimate Tensile Strength, YM = Young's Modulus.

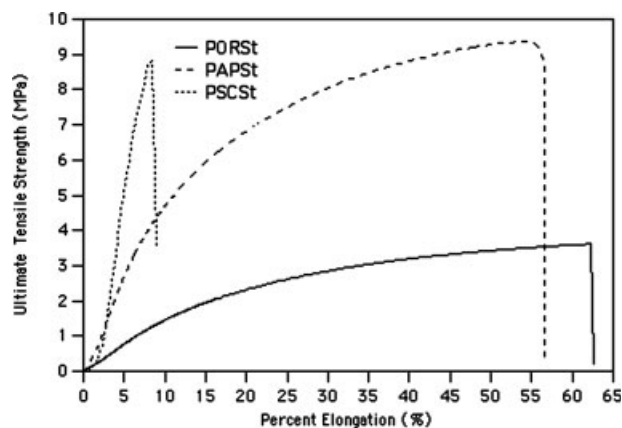


Figure 2 Mechanical traces of PORSt, PAPSt, PSCSt.

substituted with OR in this formulation, like in PORG, leaching of glycerol was no more observed. The substitution of starch with orange waste in hybrid composite based on PVA and glycerol presented a modest variation in mechanical properties. Thus for PStG and PORG elongation at break (EI), ultimate tensile strength (UTS) and Young modulus (YM) presented comparable values as reported in Table III.

To reduce as much as possible the amount of the synthetic material in the composites, a mixture was prepared with a 150/100/100/100, PVA/Starch/Orange/glycerol ratio (PORSt). The comparison of PORG with PORSt mechanical properties suggested that the introduction of starch in the formulation decreased moderately mechanical properties.

PORSt was compared with the same formulation based on sugar cane (PSCSt) and apple wastes (PAPSt). The stress to strain curve expressed by ultimate tensile strength versus percent elongation of PORSt, PAPSt, and PSCSt are compared in Figure 2.

Composites prepared with AP (PAPSt) presented similar EI values (61%), to composites prepared with OR (PORSt), but higher UTS (9 MPa) and YM (57 MPa). PVA/SC resulted also harder with a reduced EI (6%) than PVA/OR and PVA/AP composites, but with a relatively high UTS (8 MPa) and YM (171 MPa). This behavior is connected with the fillers composition and type; both AP and SC have fibrous shape that confers hardness to the composite

TABLE IV  
Impact Properties in Composites Based on PVA and Lignocellulosic Fillers

Sample	Peak energy (Joule)	StDv	Total energy (Joule)	StDv
PStOR	2.3	0.4	3.7	0.5
PStAP	3.1	0.6	6.9	0.9
PStSC	1.5	0.3	3.6	0.5

StDv = Standard Deviation.

**TABLE V**  
Composition of Samples Used in the Respirometric Degradation Test

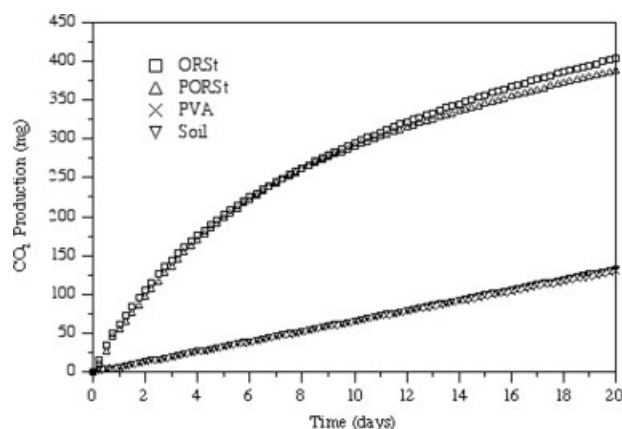
Sample	PVA (%)	OR (%)	Starch (%)	Glycerol (%)
PStOR	33.3	22.2	22.2	22.2
PVA	100	–	–	–
StOR	–	33.3	33.3	33.3

as observed in similar composites of PVA and natural fibers<sup>22,30</sup> and also with nanotubes.<sup>31</sup>

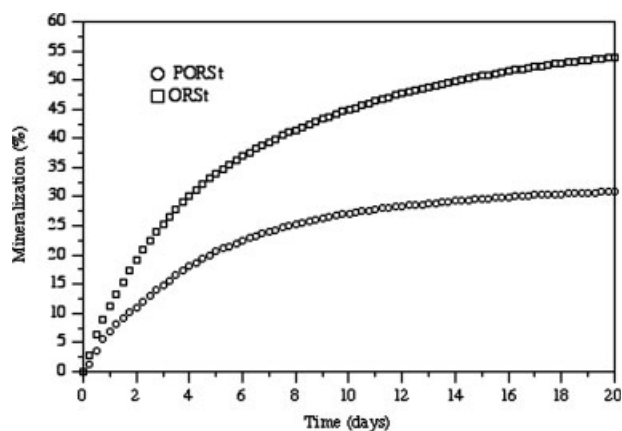
Impact test was performed on PORSt, PAPSt, and PSCSt composites. The maximum values for energy (peak energy) in the curve Load (KN)/Deflection (mm) and the total energy of the peak were recorded and are reported in Table IV. The higher values for energy at peak and total energy were recorded for PAPSt. It resulted interesting to evidence that with this processing technology (compression molding) the reinforcing effect of hard fibers is enhanced in comparison with casting by water suspension. In that case the random distribution of fibers with formation of fibers agglomerate depressed UTS for composites based on AP and SC in comparison with OR.<sup>24</sup>

In consideration of the interest in these materials for single use application to be researched mainly in the agricultural field, such as transplanting pots, etc, the effect of the addition of a nitrogen source, such as urea, in the formulation has been investigated. When urea was introduced in the formulations, special care had to be applied. If too high temperature or a relatively long time of processing were applied urea decomposed and the produced composites smelled of ammonia and resulted extremely hard and brittle.

Composites containing urea presented a higher EI as expected for the increased percentage of plasticizers additives. PORStU presented a high EI (148%),



**Figure 3** Time variation of the CO<sub>2</sub> production of PVA/OR blends in compost soil degradation test.



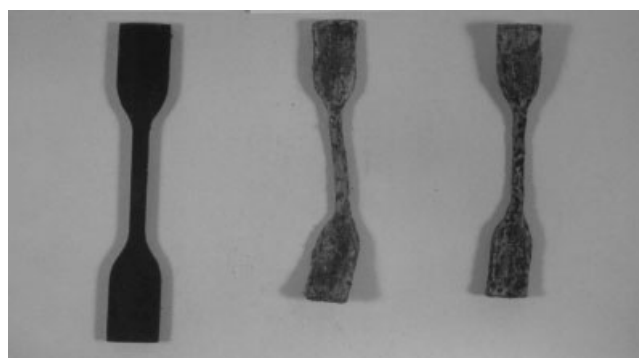
**Figure 4** Time variation of the extent of mineralization of PVA/OR blends in compost soil degradation test.

and decreased UTS (1 MPa) and YM (2 MPa) in comparison with PORSt.

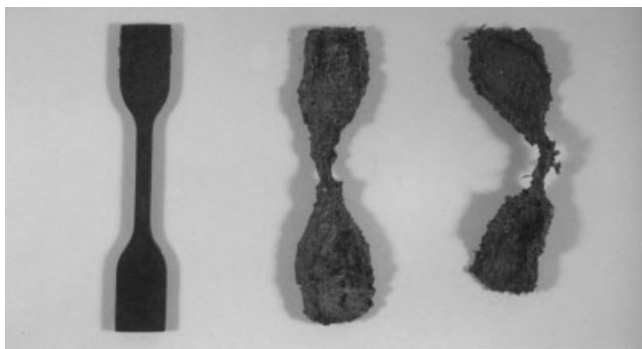
#### Respirometric degradation test

This test was performed to estimate mineralization rate of specimens prepared from the melt by compression molding. Processing from the melt enhanced PVA/fillers adhesion and favored interactions among the components. PORSt (500 mg) was selected for this test and compared with the constituting pure PVA (165 mg) and additives labeled as ORSt (335 mg). Specimens were dried, grinded and mixed with the compost soil. Compositions of the samples used for the respirometric test are reported in Table V. The four replicates for each sample presented values fluctuation of about 2%.

In this test the large CO<sub>2</sub> production from the compost soil did not allow to separate PVA production, also in consideration of the limited amount of PVA used. The CO<sub>2</sub> productions for one replicate of soil, PVA, PORSt, and ORSt are shown in Figure 3. PVA and soil productions are almost exactly over-



**Figure 5** Picture of PStOR dog bones after 0, 30, 60 days of simulated soil burial.



**Figure 6** Picture of PStORU dog bones after 0, 30, 60 days of simulated soil burial.

lapping, thus suggesting a very low mineralization of PVA. PVA resistance to degradation under soil burial conditions is in agreement with previous reports.<sup>11,14,23</sup> PVA has been shown to degrade in a liquid medium supplemented with PVA-degrading microbes.<sup>32,33</sup> But resulted fairly resistant to degradation in medium without supplemented microbes.<sup>34</sup> Ishigaki et al.<sup>35</sup> in recent study on PVA/Starch plastic degradation in activated sludge, observed that PVA degradation occurred only if PVA-degrading bacterium and/or enzyme were added to the sludge and attributed this behavior both to the rare presence of PVA bacteria in natural environment than to the long period necessary to enrich them to exhibit PVA degrading activity.

It has also been reported that the addition of PVA in starch-glycerol blend lowered both the rate and extent of blend degradation.<sup>36</sup> Interestingly about the same CO<sub>2</sub> production was recorded for PORSt and ORSt, thus indicating that in this hybrid composite the PVA presence has no negative effect on the natural components degradation. Even if as showed in Figure 1, the fillers are embedded and covered by the synthetic PVA matrix. Thus in investigating the supposition that the presence of a certain amount of natural polymers in blends with synthetic polymers can promote the degradation of the synthetic component, lignocellulosic fillers appeared particularly promising.<sup>37</sup>

Figure 4 reports the time variation of the extent of mineralization of the investigated samples evaluated as the percentage of the theoretical CO<sub>2</sub> production.

After 20 days of experiment the blend (PORSt) reached a 31% mineralization in comparison with 54% mineralization for the fillers (ORSt). These values confirmed the rapid degradation of the natural components (starch and OR) and the not yet started degradation of the synthetic polymer fraction.

### Soil burial test

A soil burial test was carried out on dog bone specimens of compression molded samples, to evaluate the loss of mechanical properties and weight loss of the blends after different periods of permanence in soil, respectively, 30 and 60 days. PORSt and PORStU samples were selected for this test. Figures 5 and 6 show respectively, PORSt and PORStU before and after 30 and 60 days of burying.

After just 1 month of burial, the specimen morphology changed significantly. Specimens were appreciably altered and substantial weight-losses were detected for all samples as reported in Table VI. The soil contamination and microbial debris adhered to the buried specimens could potentially impact the weight loss data. Visually, specimens containing urea (PStORU) appeared more deteriorated, thus their size and shape and surface area were remarkably increased. Urea is considered a limiting factor in soil and water environments. Added urea in formulations represented an additional nitrogen source for microorganism and helped expedite the degradation process. In specimens buried for 30 and 60 days only small differences were observed indicating that microbial and/or enzymatic activities have subsided.

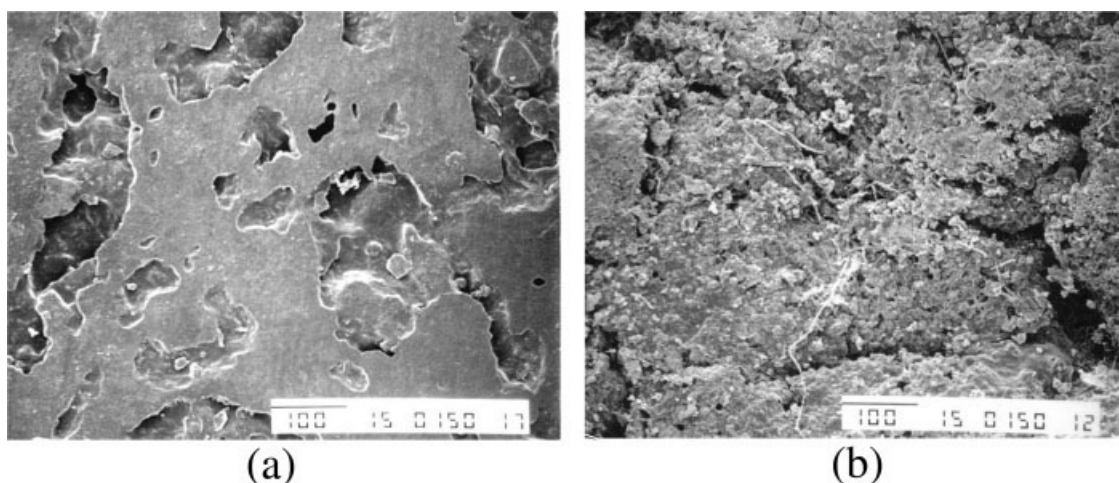
All buried specimens showed a decrease in El between 70 and 80%, and a severalfold (3–4 times) increase in UTS. Such change in mechanical properties can be attributed to the loss of plasticizer and the physical deterioration of the specimens (Table VI).

After 1 (or 2 months) of soil burial, specimen appeared deteriorated with rough surface [Fig. 7(a,b)]. The extensive growth of actinomycetes and fungi on the surface was quite apparent (Fig. 8). It was interesting as well as significant to note that the colonization of actinomycetes occurred not only on

**TABLE VI**  
Variation of Weight and Mechanical Properties of PORSt and PORStU in Dependence of Soil Burial Time

Sample	Burial (days)	Weight loss (%)	El (%)	StDv	UTS (MPa)	StDv
PStOR	0	–	56	2	3.4	0.1
	30	45	12	2	14.0	1.0
	60	50	11	1	14.0	1.3
PStORU	0	–	148	22	1.2	0.1
	30	39	45	8	3.5	0.7
	60	46	45	9	4.0	1.1

El = Elongation at Break, UTS = Ultimate Tensile Strength.



**Figure 7** SEM micrograph ( $\times 500$ ) of PStORU surface after 0 (a) and 60 (b) days of simulated soil burial.

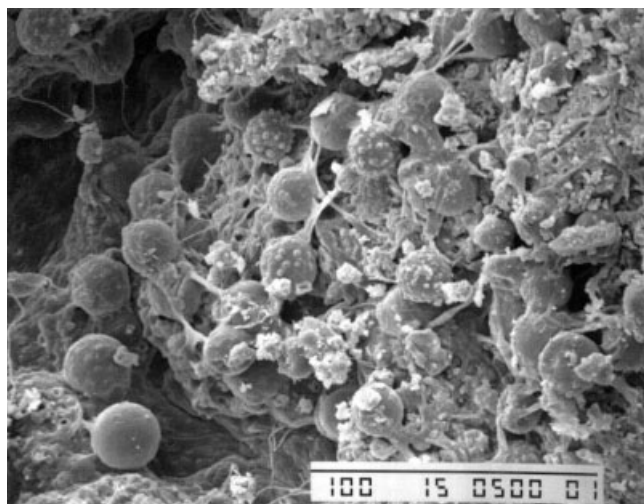
the surface of the samples, but the organisms were able to penetrate into the interior (bulk) of the composite. SEM clearly shows the presence of actinomycetes inside the voids of PORSt and PORStU (Fig. 9). Migration or entrapment of microorganisms in the voids in the interior of the samples could certainly help stimulate the material degradation upon disposal.

### CONCLUSIONS

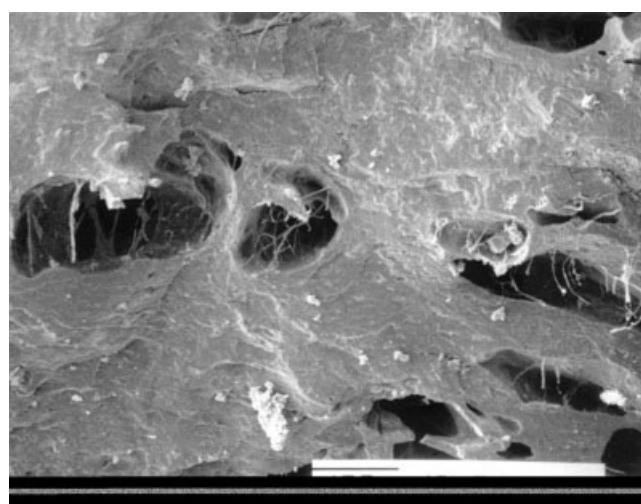
PVA and lignocellulosic fillers produced cohesive and homogeneous composites by processing from the melt with fibers content up to 22% by weight, in the presence of water (about 60% on dry weight) and glycerol (about 20% of dry weight). Mechanical properties of the prepared composites were dependent from fibers type and plasticizers content. Thus

blends prepared with AP and SC resulted harder than blends prepared with OR. Young's modulus was 15 MPa for PORSt, 57 MPa for PAPSt and 171 MPa for PSCSt. The introduction of starch in the formulation decreased moderately mechanical properties while an increase of the amounts of natural fillers increased degradation and reduced cost of the final product. Respirometric test revealed that soil microbes preferentially used natural polymers and low molecular weight additive as a carbon source compared to biodegradable synthetic polymer. The presence of PVA in formulations had no negative effect on the degradation of lignocellulosic fillers. The limited PVA mineralization recorded in the experiment time can be attributed to a too short time of the burial test or at the absence of PVA degrading bacteria.

PVA/OR specimen buried in the soil exhibited about 50% weight loss and substantial deterioration



**Figure 8** SEM micrograph ( $\times 500$ ) of fungi present on PStORU surface after 30 days of simulated soil burial.



**Figure 9** SEM micrograph ( $\times 150$ ) of PStOR fracture after 30 days of simulated soil burial.

in mechanical properties extensive Growth of micro-organisms was observed on the surface and in the interior of the specimen.

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