Macromol. Symp. **152,** *83–94 (2000)*

Environmentally sound blends and composites based on water-soluble polymer matrices

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SUMMARY: The realization of plastic items intended to not constitute an environmental burden once they become waste or simply post-consume products represents the main goal of a research project focused on the utilization of water-soluble synthetic polymer, e.g. poly(vinyl alcohol), and natural raw materials for the preparation of cast films and composites. A series of plastic sheets and films were obtained from water solution and dispersion of poly(vinyl alcohol) and waste gelatin, as well as from blends of the vinyl polymer with lignocellulosic materials such as sugar cane bagasse. Thermal properties of the films, as well as their biodegradation behavior under different incubation conditions, and in particular under soil burial conditions, were investigated with the aim of identifying the compositions best suited to obtain films and composites suitable for agricultural applications.

Introduction

The use of Environmentally Degradable Plastics (EDPs), and in particular biodegradable plastics in agricultural and waste management applications is one of the key issues to preserve soil fertility and environmental safety, often burdened by economical problems. It is well known that recycling procedures can face insurmountable technical problems in these areas.

Since a few years, we have been involved in the preparation of multifunctional hydrophilic polymers starting from synthetic as well as from naturally occurring products(1-3). Particular attention is currently being devoted to the utilization of materials from renewable resources such as agricultural over-productions and by-products, as well as waste materials. In this connection, the preparation and characterization of polymer composites and blends based on water soluble polymers such as poly(vinyl alcohol) (PVA), pharmaceutical grade waste gelatin (WG) and lignocellulosic agricultural by-products such as sugar cane bagasse (SCB), was carried out. Both the continuos polymeric phases of synthetic origin (PVA) and

CCC 1022-1360/00/$ 17.50+.50/0

from natural resources (WG) as well as the organic filler (SCB) are meant to be bioconverted to harmless intermediates eventually susceptible to full mineralization by microorganisms.

PVA, one of the few synthetic polymers with a truly biodegradable, non heteronuclear backbone$^{4-7)}$, displays characteristics, such as water solubility, gas barrier properties, filmability, and mechanical properties that have attracted increasing attention for the preparation of polymer blends with different polyhydroxylated compounds$^{8,9)}$. In particular several examples of PVA/starch$^{10,11)}$ and PVA/cellulose$^{12)}$ blends have been reported in the literature and their biodegradability has been thoroughly investigated under different environmental conditions. However, little information are available on PVA biodegradation when used as major component or continuos phase in blends and composites, respectively. This in particular holds true for degradation experiments carried out in simulated or real soil burial tests$^{10,13)}$ reproducing the conditions in which the blends and composites obtained by casting or spraying from water solution or dispersion are intended to exploit their service life. Accordingly, an extensive investigation of both thermal and biodegradation properties of the prepared plastic films have been carried out and the obtained results constitute the body of the present contribution.

Results and discussion

Agricultural lignocellulosic by-products such as sugar cane bagasse (SCB), as well as waste gelatin (WG) from the pharmaceutical industry, were utilized for the preparation of polymer blends and composites by using PVA (degree of hydrolysis 88 %) as major component or continuos phase. Composite plastic sheets were obtained by mixing of the different water solutions and/or dispersions, prepared by solubilization or suspension of each component in water, followed by casting at room temperature. In a few cases, urea was added to the composite mixture, to act as a sustained release fertilizer. A low molecular weight plasticizer (glycerol) and a crosslinking agent (glutaraldehyde) were also tested respectively to modulate the film thermal and mechanical properties and to improve film coherence and water resistance.

The compositions of the investigated preparations expressed as weight percent of dry materials are reported in Tab. 1.

The thermal properties of the samples were analyzed by differential scanning calorimetry

(DSC) and thermogravimetric analysis (TGA). The starting raw materials and films obtained by casting PVA water solutions were also analyzed for comparison.

In Fig. 1 the DSC traces of a waste gelatin/PVA blend (sample GP) are compared to those of a PVA cast film and of pure waste gelatin (WG).

Tab. 1. Composition of polymer blends and composites[a)]

Sample	PVA/wt %	SCB/ wt %	WG /wt %	UR/ wt %	GLY/ wt %	GLU/ wt %
PX	100	0	0	0	0	0.25
BP	50	50	0	0	0	0
BPUG1	33	33	0	17	17	0
BPUG2	33	33	0	17	17	0
GP	80	0	20	0	0	0
GPX	80	0	20	0	0	0.25
GPB	67	16.5	16.5	0	0	0
GPBX	67	16.5	16.5	0	0	0.25

[a)] PVA: poly(vinyl alcohol), SCB: sugar cane bagasse, WG: waste gelatin, UR: urea, GLY: glycerol, GLU: glutaraldehyde.

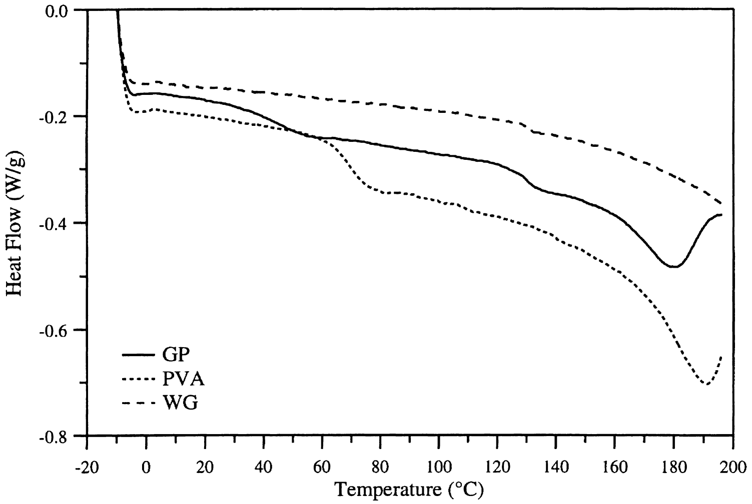

Fig. 1: DSC traces of PVA/gelatin blend (sample GP), poly(vinyl alcohol) cast film (PVA) and pure waste gelatin (WG)

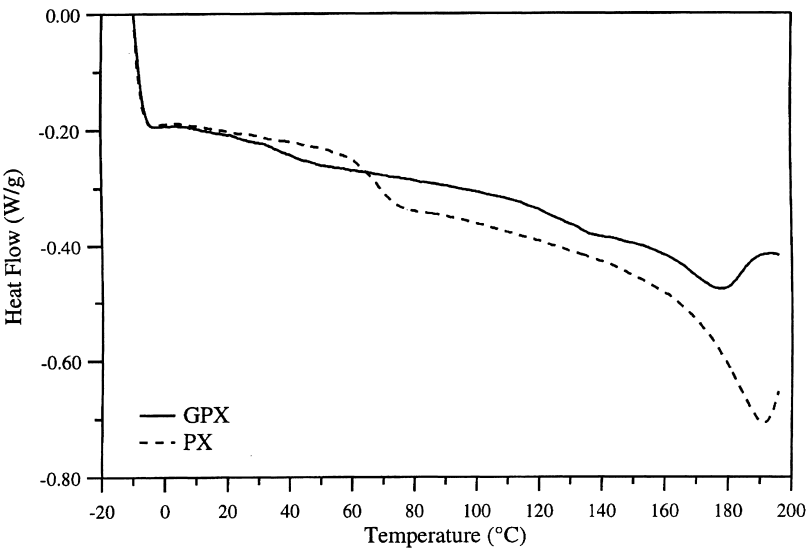

Fig. 2: DSC traces of PVA/WG (GPX) and PVA (PX) films containing 0.25 % by weight of glutaraldehyde as crosslinking agent

Addition of glutaraldehyde as crosslinking agent, did not appreciably affect the thermal properties of both PVA and PVA/WG blends (Fig. 2).

In the case of PVA/SCB composites, the presence of a large amount of the heterogeneous and water insoluble lignocellulosic material, seems to promote an increase of the Tg relevant to PVA component from 50-55 to 65-70 °C (Fig. 3).

As shown, the PVA film is characterized by a glass transition and a melting peak respectively at 70 and 191 °C. A weak but definite glass transition can be observed at 137 °C in the DSC of WG sample. The DSC profile of GP blend film exhibited two glass transitions and an endothermic peak respectively at 47, 131 and 182 °C, approximately in correspondence with those of the individual components present in the blend. The lower value of the glass transition temperature (T_g) and the melting temperature recorded for the PVA component in GP blends with respect to pure PVA denote the plasticizing effect played by the WG component[14).

The T_g increase and the heterogeneity of the composite make this material brittle and provided with moderate strength, as indicated also by mechanical property testing. Indeed, the tensile strength of the 1:1 PVA/SCB composite resulted to be 3.6 MPa, a value one order of magnitude lower than that of PVA cast films (36 MPa).

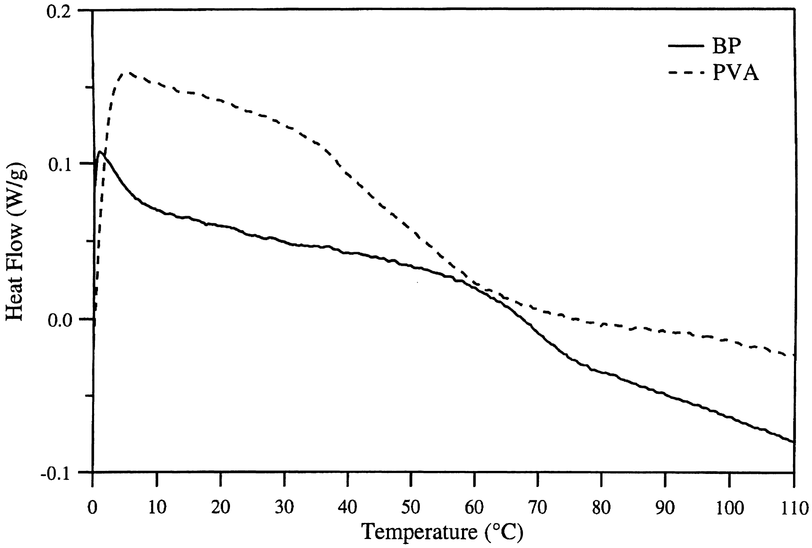

Fig. 3: DSC profiles of 1:1 PVA/sugar cane bagasse blend (sample BP) and PVA cast films

TGA analysis confirmed that the thermal stability of PVA (T_{on} 279 °C) is appreciably larger than that of WG (T_{on} 232 °C) and SCB (T_{on} 220 °C), as expected from their respective chemical structures. However, blends of the synthetic polymer with either WG (T_{on} 263 °C, Fig. 4) or SCB (T_{on} 267 °C, Fig. 5) exhibited only a modest decrease of the onset of the decomposition temperature as compared to pure PVA. The large decrease of thermal stability observed for BPUG samples (T_{on} 197 °C) must be attributed to the initial loss of low molecular weight components (urea and glycerol).

However, these blends still possess the characteristics of thermoplastic materials and they should be processable by injection molding by taking into account that in all cases the onset of the decomposition process occurs at temperatures at least 30-50 °C higher than the processing temperature. On the contrary, the presence of a large amount of low molecular weight additives, such as urea and glycerol, whose volatilization occurs at about 160 °C, can represent a serious obstacle for the blend thermal processability.

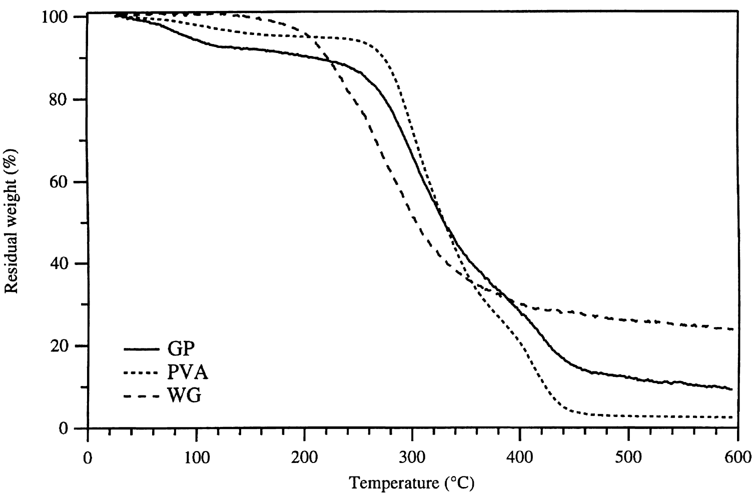

Fig. 4: TGA traces of 8:2 PVA/WG blend (GP), waste gelatin (WG) and PVA cast films

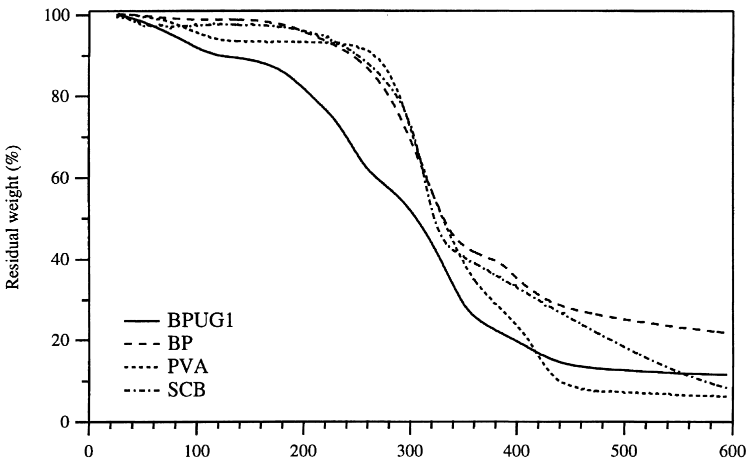

Fig. 5: TGA traces of 33:33:17:17 bagasse/PVA/urea/glycerol blend (sample BPUG1), 1:1 bagasse/PVA blend (sample BP), PVA cast films, and sugar cane bagasse (SCB)

Biodegradation studies of the prepared polymer blends and composites were carried out both in liquid and solid cultures by using respirometric determinations to assess their extent of mineralization.

The biodegradation of different PVA/SCB and PVA cast films was investigated in aquatic aerobic biodegradation tests by using selected PVA-degrading microbial strains as inoculum[15]. As shown in Fig. 6, significant degradation levels were reached in cultures supplemented with either PVA or PVA/SCB blends. The largest extent of biodegradation (45 %) was detected in the case of pure PVA film, as expected from the specificity of the utilized microorganisms. However, large mineralization levels (30-35 %) were observed also for PVA/SCB blends, whereas SCB was only partially assimilated (17 %) by PVA-degrading microorganisms.

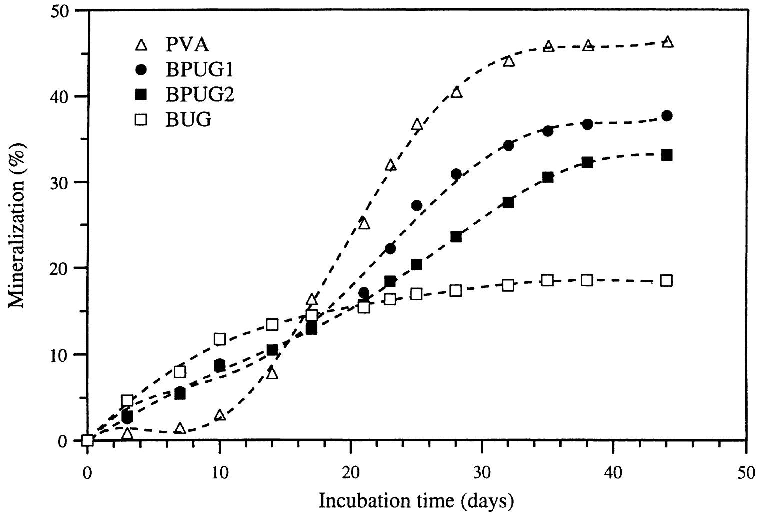

Fig. 6: Biodegradation curves of SCB/PVA/urea/glycerol blends (samples BPUG1 and BPUG2), PVA cast films and SCB/urea/glycerol (BUG) in aquatic aerobic biodegradation tests

Since the investigated blends and composites of PVA with raw and waste materials were formulated for their utilization as agricultural mulching films, further biodegradation studies were carried out under conditions aimed at simulating soil burial tests. Experiments were performed according to an innovative respirometric procedure developed in our laboratory to evaluate the mineralization of polymeric compounds in the presence of soil microorganisms16). In the adopted experimental set-up (Fig. 7), most of the soil is replaced by an hygroscopic aluminosilicate (perlite) in order to limit the amount of CO_2 produced by soil with respect to the investigated samples and thus maximize the signal-to-noise ratio.

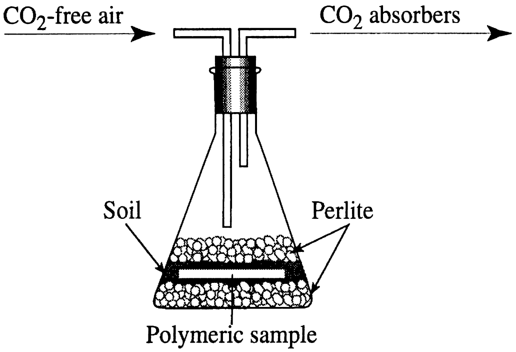

Fig. 7: Experimental set-up adopted in the simulated soil burial degradation tests

Under the adopted conditions, SCB underwent a rather intense degradation process, reaching 35 % mineralization after 5 months of incubation. This value compares fairly well with the 50 % degradation shown by a cellulose sample utilized as reference material (Fig. 8). Within the same time frame, the PVA/SCB sample underwent a lower (20 %) but still significant mineralization as mediated by soil microflora.

A similar behavior was observed in simulated soil burial tests of PVA/waste gelatin blends that reached a 30-35 % degree of mineralization after 30 days (Fig. 9). Comparable levels of biodegradation were detected for films containing both SCB and WG (GPB sample). During the same incubation time a WG sample underwent extensive mineralization (57 %), whereas the cellulose reference sample was only partially degraded (25 %).

Addition of 0.25 % of glutaraldehyde as crosslinking agent had a very limited influence on the rate of degradation, a small negative effect being observed only in the case of PVA/WG blends (sample GPX) (Fig. 9). In all cases, the presence of PVA strongly depressed the rate and extent of biodegradation of the natural component of the blends in soil burial tests.

Accordingly, very little degradation of pure PVA occurred under soil burial conditions, in agreement with previous reports[10,17,18], very likely due to the irreversible adsorption of PVA on soil components[19,20]. Indeed, analogous absorption phenomena completely inhibit the enzymatic degradation of polysaccharides[21] and proteins[22].

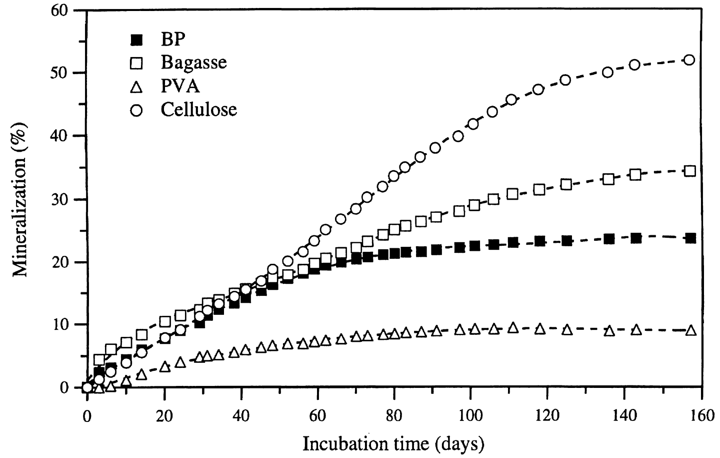

Fig. 8: Biodegradation curves of PVA/SCB (1:1 blend, sample BP), PVA cast films, sugar cane bagasse and cellulose in simulated soil burial degradation tests

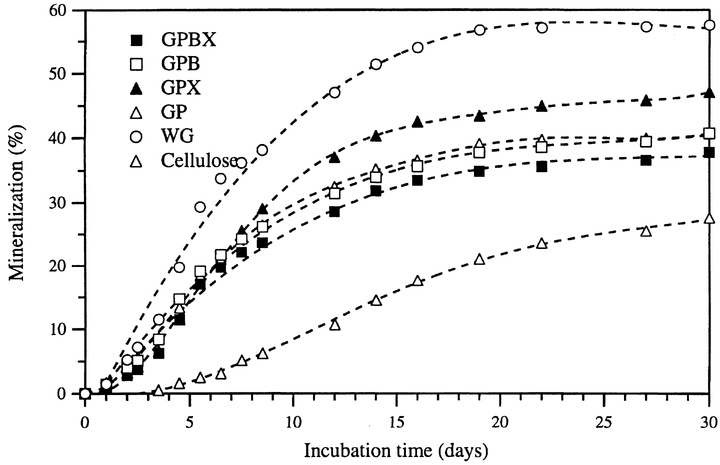

Fig. 9: Biodegradation curves of different PVA/waste gelatin/sugar cane bagasse blends, waste gelatin (WG) and cellulose in simulated soil burial degradation tests

At the end of simulated soil burial tests, some residual debris were recovered in the case of PVA/SCB and PVA/SCB/WG composite films whereas PVA/WG blend samples apparently vanished from the soil layer.

SEM analysis of both PVA/SCB and PVA/SCB/WG specimens before and after the degradation tests highlighted that the PVA/WG homogeneous phase completely disappeared following biodegradation and/or dissolution of gelatin and PVA, leaving a loose network of bagasse hard fibers (Fig. 10).

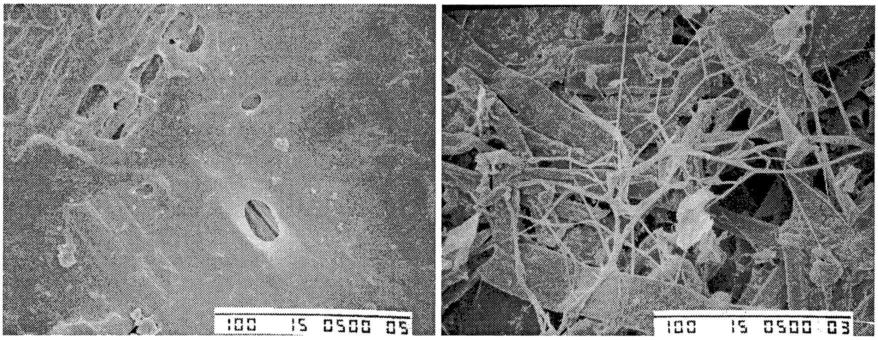

Fig. 10: SEM micrographs (500X) of PVA/SCB/WG composite before (left) and after (right) the simulated soil burial degradation test

Conclusions

Blends and composites, based on water soluble synthetic and natural polymeric material as well as lignocellulosic agroindustrial by-products, were prepared by a simple casting procedure of water solutions and/or dispersions. By this technique rather thin coherent films were obtained that were characterized by thermal and mechanical analysis. Their biodegradation behavior was also investigated under different environmental conditions.

We have found that mechanical properties as well as degradation rate and extent of the investigated blends and composites can be modulated by suitably tuning their chemical composition. In addition, the different components of the blends might exert a beneficial role on soil structure and fertility.

Indeed, PVA can be used as a soil conditioner23,24), whereas sugar cane bagasse and waste gelatin represent a humic substance source and a nitrogen fertilizer, respectively. Moreover, the presence of fillers helps making the PVA composite films permeable to liquid water, while maintaining an appreciable degree of integrity, thus offering an indisputable advantage in the watering of soils eventually mulched by these films.

These results highlight the large potential of the investigated blends and composites in agricultural application as self fertilizing mulching films.

Acknowledgements

The partial financial support by CNR and MURST is gratefully acknowledged. The fellowship granted by ICS-UNIDO to E.-R. K., within the subprogram on Environmentally Degradable Plastics, is also acknowledged.

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