Macromol. Symp. **2003**, *197*, 143—155

Characteristics and Degradation of Hybrid Composite Films Prepared from PVA, Starch and Lignocellulosics

Patrizia Cinelli,[1] *Emo Chiellini,**[1] *Sherald H. Gordon,*[2] *Syed H. Imam*[2]

[1] UdR – INSTM Consortium @ Department of Chemistry & Industrial Chemistry, University of Pisa, Via Risorgimento 35, 56126 Pisa, Italy
[2] Plant Polymer Research Unit, National Center for Agricultural Utilization Research, Agricultural Research Service, USDA, 1815 North University Street, Peoria, IL 61604, USA

Summary: A research cooperation between USDA and the University of Pisa led to the development of several composite blends of poly(vinyl alcohol) (PVA) and lignocellulosic fibers. The cast films were prepared by blending orange fibers (OR-fibers) and PVA with and without cornstarch to yield flexible and cohesive films. To improve properties, films were also prepared by crosslinking PVA, starch and OR-fibers with hexamethoxymethylmelamine (HMMM). Films were evaluated for their thermal stability, water permeability and biodegradation. Thermal gravimetric analyses indicated the potential usefulness of such blends in several thermoplastic applications. Films were permeable to water, and retained the moisture content in the soil while retaining their integrity. Films generally biodegraded within 30 days in compost, achieving between 50-80% mineralization. Both neat PVA and blends that had been crosslinked showed comparatively slow degradation. A possible stimulating effect of lingocellulosic fillers on the biodegradation of PVA in blends has been observed.

Keywords: biodegradation; composites; fillers; poly(vinyl alcohol); renewable resources

Introduction

Plastic materials are commonly used in agricultural practices for several types of applications that include mulch films, greenhouse construction and packaging materials [1]. Most of the plastics used are petroleum-based synthetic chemicals that do not degrade when disposed in the environment after their useful life is over. As a result, interest in the use of degradable and biodegradable polymers in plastics for agriculture application has grown considerably in recent years [2,3]. Currently, efforts are being made to develop environmentally compatable plastic products by incorporating renewable biopolymers as an alternative to petroleum-derived chemicals [4,5]. The renewable polymers are relatively inexpensive, environmentally friendly, and

DOI: 10.1002/masy.200350714

also naturally biodegradable. Particularly, plant material derived from renewable crops, by-products or their industrially processed wastes is a good source of fiber for applications [6]. Ongoing research cooperation between USDA and the University of Pisa, Italy has led to the development of several composite blends of poly(vinyl alcohol) (PVA) and lignocellulosic fibers derived from the wastes of industrially processed sugar cane bagasse, apple, and oranges (OR) [7]. PVA is well suited for blends with natural polymers since PVA is highly polar and can also be manipulated in water solutions [8-10]. This paper describes the continued research on hybrid cast films prepared by blending OR-fibers with PVA. Films were cast from aqueous suspensions with and without hexamethoxymethylmelamine (HMMM) present as a crosslinking agent. Urea and glycerol were added as plasticizers. Additionally, cornstarch was added in the formulation to further increase the content of renewable polymers and to reduce the production cost of the films. PVA/OR hybrid composites are under consideration for agricultural application such as mulch films, greenhouse construction and packaging materials, transplanting sacks or pots. The extrusion and injection-molding of these materials is currently being carried out in several laboratories including ours. Thus, to develop understanding of these materials, fundamental research is warranted. In particular, these materials need to be evaluated for their thermal properties, water permeability and biodegradability, as well as for the impact on their properties due to blending with other polymers.

Materials and Methods

Poly(vinyl alcohol) (PVA Airvol 425) was purchased from Air Products & Chemicals Inc., Allentown. PVA Airvol 425 was 95.5-96.5% hydrolyzed with an average molecular weight of 100,000-146,000. Hexamethoxymethylmelamine (HMMM, Cymel 303) is a low imino melamine-formaldehyde crosslinking agent with a D.P. of 1.75, an average degree of methylation of 97%, and was purchased from Cytec Industries. Inc., Wallingford, CT. Citric acid was obtained from Aldrich Chemical Company, Milwaukee, WI. Glycerol and urea were purchased from Fisher Chemicals, and Sigma Chemical Company, St. Luis, MO, respectively. Unmodified commercial-grade cornstarch (Buffalo 3401) with approximately 23% amylose and 77% amylopectin was obtained from CPC International Inc., Argo, IL. Orange fibers (OR) were the remains of fruit residue after juice extraction, supplied by the Sunflo Cit-Russ Limited, Lahore, Pakistan, milled and sieved to obtain 0.188 mm size particles. OR composition was: 18% Cellulose, 13% protein, 15% crude fiber, 7% fat, 5% lignin, 11% ash, 21% hemicellulose and/or pectins, and 10% moisture.

Sample Preparation

A predetermined amount of PVA was added to water to achieve a solution of 10% solid content. The mixture was slowly heated to about 90°C with stirring until a homogeneous solution was formed. Water was added to compensate for any moisture loss that may have occurred during the heating process. In a 250 ml beaker, about 62 g of PVA solution was introduced and the desired amount of glycerol, urea, starch and water was added (by weight) to give a final concentration equivalent to 10% solids. The resulting mixture was first heated at 80°C for 30 min under stirring and 6.2 g of OR was added. The mixture was stirred for an additional 10 min.

For crosslinked samples, a desired amount of HMMM and a catalytic amount of citric acid were also added in formulations and the resulting mixture was stirred at 70°C for 45 min. After cooling at room temperature, 3 drops of BYK-019 aqueous defoamer was added and the mixture was further stirred for 5 min. Table 1 provides the description of blends and their compositions.

To prepare films, about 17 g of aqueous suspension (as described above) was poured into a polypropylene plate (8 x 8 cm) and left to dry overnight at ambient temperature (23-24 °C) and finally for 3 h in an oven at 50 °C.

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°C to 600°C at a 10 °C/min scanning rate, under nitrogen atmosphere (flow rate about 200 ml/min). The onset temperature (T_{on}) was determined as the temperature corresponding to the crossover of tangents drawn on both sides of the decomposition trace and the residue was evaluated as the residual weight at 600 °C.

Water Permeability

Water permeability was assessed by using 6 cm diameter Fisher Payne permeability cups containing 5 ml of water, sealed with the selected films. Caps were stored in a conditioned room (23°C and 50% RH) and variation with time of water weight was recorded. Tests were performed in triplicate. Three caps were sealed with poly (ethylene) (PE) as negative reference.

Films Deterioration on Soil

Cast films were cut in small squares (3x3cm). Each specimen was placed in agricultural soil in a 6 x 6 cm pot. The pots were covered with plastic mesh and exposed to ambient conditions for 4 months in the vicinity of University of Pisa, Pisa, Italy. Variations in film morphology and disintegration time were recorded.

Soil Burial Respirometric Test

About 500 mg of PVA/OR blends (Samples PStOR, PORX) and the corresponding amounts of PVA (150 mg) and additives (350 mg samples StOR, StORX) were cut into small pieces (2 x 2 mm) and 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. The sample chamber was placed in the water bath thermostated at 25°C and connected to the Micro-Oxymax respirometer. The cumulative CO_2 evolution was recorded every 6 h. Experiments were carried out over a period exceeding 55 days.

Result and Discussion

Based on earlier studies with PVA and lignocellulosic fiber composites[11] selected samples were prepared by blending PVA and starch with or without crosslinking with hexamethoxymethylmelamine. Samples of hybrid composites were designated as (Table 1) PVA/starch (PSt); crosslinked PVA/starch (PStX); PVA/starch/OR-fibers (PStOR); crosslinked PVA/starch/OR-fibers (PStORX) and, PVA/OR-fiber without starch but with glycerol and urea (PORGU).

Table 1. Composition of Hybrid Composite Films Based on PVA/Starch and PVA/OR

Sample	PVA (wt-p)	Fibers (wt-p)	Gly (wt-p)	Urea (wt-p)	Starch (wt-p)	HMMM (wt-p)	CitAc (wt-p)
PSt	100	-	50	50	50	-	-
PStX	100	-	50	50	50	29	2.9
PStOR	100	100	50	50	50	-	-
PStORX	100	100	50	50	50	29	2.9
PORGU	100	100	50	50	-	-	-

Gly = Glycerol, HMMM = hexamethoxymethylmelamine, CitAc = Citric Acid, wt-p = weight parts, Samples: P = PVA, St =Starch, X = Crosslinked, POR series based on orange (OR) as filler, G =Glycerol, U = Urea.

Thermal Characteristics

Thermal gravimetric analysis (TGA) of samples was performed to define and compare thermal stability of the starting raw materials and the film obtained from the aqueous suspension of blended materials. In the degradative curves for OR-fibers in Figure 1, at least two decomposition steps are recognizable at 249°C and 305°C, respectively.

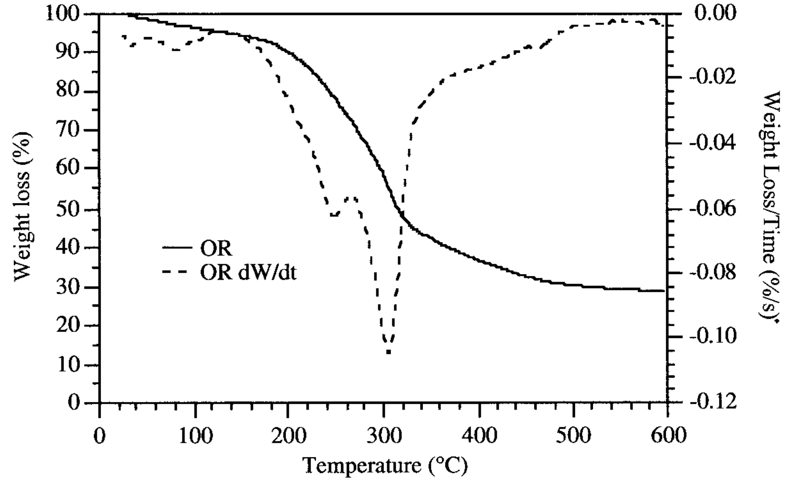

Figure 1. Decomposition trace and first derivative of OR-fibers degradation curve

Expectedly, the presence of multiple decomposition peaks in OR-fiber appears to be in accordance with the composite characteristics of the materials. Because thermal decomposition of the prepared blends depends on the thermal stability of each component present in the mixture, the thermal stability of PVA, starch, glycerol, and urea was analyzed individually. The results are presented in Table 2. After water loss, PVA decomposition occurred in two steps and T_{on} was observed to be at 266°C. Both starch and glycerol exhibited a single-step decomposition and the T_{on} were found to be at 277 °C and 170 °C, respectively. Whereas, urea decomposed in two steps with T_{on} at 169 °C.

Table 2. Thermal Parameters of Raw Components

Material	Volatiles (%)	T_{on} (°C)	Peak 1 T (°C)	Peak 1 WL (%)	Peak 2 T (°C)	Peak 2 WL (%)	Residue (%)
OR	5	193	249	23	305	43	29
PVA	2	266	317	76	412	17	3
Starch	7	260	296	81	-	-	12
Glycerol	1	170	247	99	-	-	0
Urea	1	169	221	64	348	35	0

OR = Orange fibers, Ton = onset Temperature, Peak1 = first decomposition peak, Peak 2 = second decomposition peak, Residue = Residue Weight % at 600 °C, T = Temperature, WL = Weight Loss.

After a water loss of about 4%, three degradations peaks were observed from the thermal profile of PStOR at 221°C, 320°C and 408°C with the T_{on} at 168°C (Figure 2).

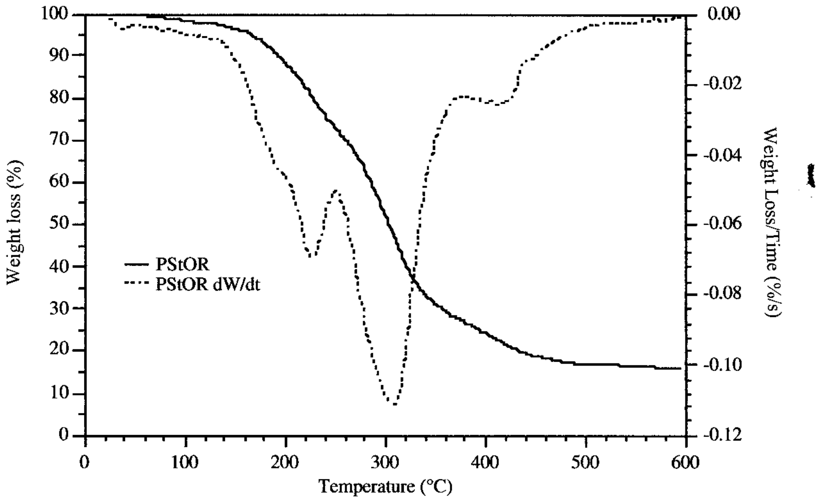

Figure 2. Decomposition trace and first derivative of PORSt degradation curve

The decrease of thermal stability observed for the hybrid composite film must be attributed to the initial loss of low molecular weight component such as urea and glycerol present in the formulation. It is particularly important that the low decomposition temperatures for the glycerol and urea must be taken into account when these materials are processed at high temperatures. The blends investigated here showed characteristics of thermoplastic materials and the degradation temperatures were found to be good enough for applications such as mulch film, greenhouse construction and packaging material. The thermal stability of PVA and OR-fiber mixtures indicated suitability of these materials for melt processing technologies.

Water Permeability

Composites tested were permeable to water vapors. Films appeared softened by water absorption but remained consistent and cohesive.

All films had a thickness of 0.3 mm, and were previously conditioned at 50% RH (23°C) for one week prior to testing. The vapor permeability is expressed as % weight of water loss in the time (Figure 3).

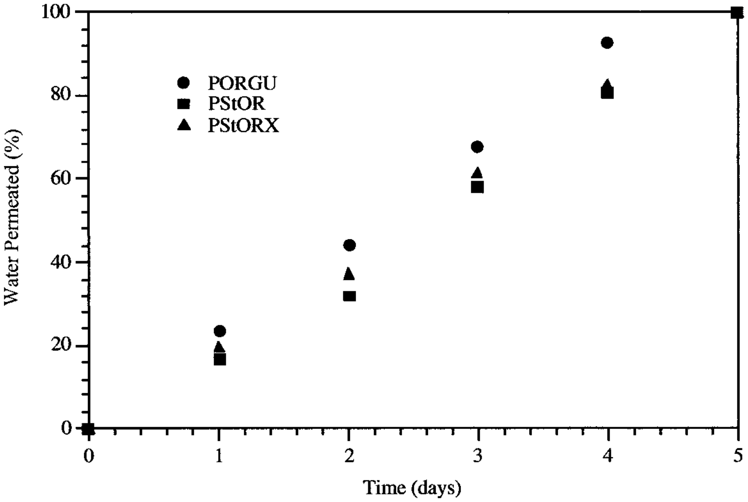

Figure 3. Water permeabilty through PORGU, PStOR, and PStORX hybrid composite films

Physical Deterioration and Biodegradation of Films

The environmental performance and biodegradation of films was evaluated by exposing film samples in soil for 120 days in the natural environment. Under wet (rainy) conditions, water penetrated through the films and the films became swollen and soft. Upon drying, however, films retained most of their cohesiveness and integrity. These observations suggest that these films when applied in fields will allow permeation of water and its subsequent retention. After 120 days of exposure in soil, specimens appeared brittle and fragile and diminished in size (Figure 4), thus indicating the natural biodegradation of these films in the soil environment and eventual composting.

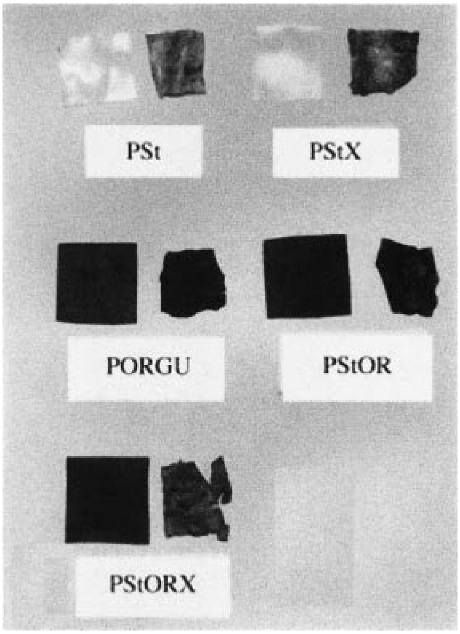

Figure 4. Control and films (PSt, PStX, PORGU, PStOR, PStORX) exposed in soil for 120 days

All films deteriorated in soil within 120 days. Particularly, all films lost weight and suffered loss in mechanical properties. Almost all films lost close to 50% of their dry weight except crosslnked (PStORX) films, which showed only 40% weight loss (Table 3). The weight losses were probably understimated due to soil and debris adhered to the film surface.

Table 3. Weight Loss of Films Exposed to Soil in Natural Environment for 4 Months

Sample[a]	Weight Loss[b]	Weight Loss[c]
(%)	(%)	
PSt	42±2	47
PStX	48±3	51
PORGU	46±2	51
PStOR	41±1	48
PStORX	35±4	41

[a] All samples were first cleaned with a brush and the weight was recorded. A specimen of each sample was quickly washed in cold water and then the sample was dried in an oven at 70°C to constant weight. The weight of the sample was recorded before and after washing. [b] recovered from the soil and cleaned with a brush. [c] after washing in cold water.

Biodegradability of Film and Components in Compost Environment

Films and their components were tested for their biodegradability in a controlled compost environment using the respirometeric method. The production of CO_2 is used as an indicator of microbial mineralization of organic carbon in a sample exposed to compost. The CO_2 produced by the PVA sample alone was essentially negligeable and was similar to the background controls containing only compost (Figure 5). About 2% mineralization was recorded for both crosslinked and uncrosslinked PVA (Figure 6). Similar observations have also been made by other investigators with regards to slow PVA degradation in soil [12-17]. Most often this is attributed to the absence of PVA-degrading micro-organisms in the soil. PVA has been shown to degrade much faster in a liquid medium suplimented with PVA degrading microorganisms [18] compared to unsupplemented water samples [19]. Interestingly, blends in which PVA was blended with starch and OR-fibers exhibited much higher CO_2 production than starch-OR-fiber blends without PVA (Figure 5). The synergistic effect of lignocellulosic fillers on the degradation of PVA is currently being examined in the laboratory.

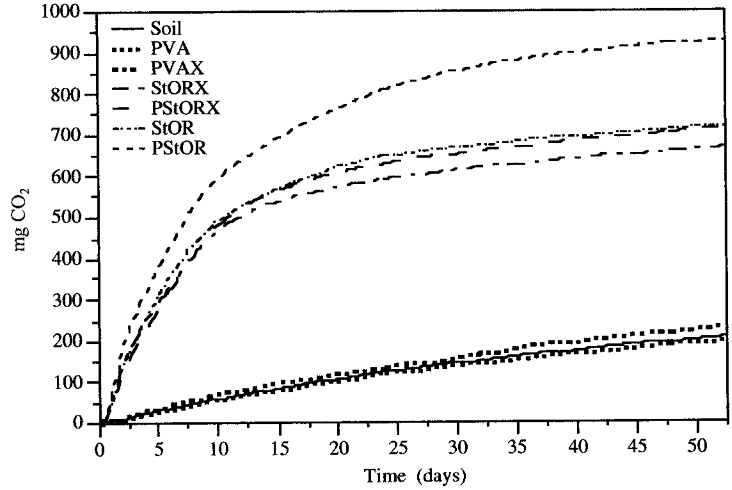

Figure 5. CO_2 Production of Soil (control), PVA, PVAX, PStOR, StOR, PStORX and StORX

The amount of CO_2 released from the additives exceeded the value corresponding to 100% mineralization (Figure 6), indicating that starch along with other additives, such as urea and glycerol, readily provided carbon and nitrogen sources which enhanced the mineralization capacity of soil. This "priming effect" is already well documented in the literature [20, 21].

Compared to lignocellulosics, urea, glycerol and starch are easily degraded and a high mineralization activity was recorded for these components.

Crosslinking generally impacted the overall material biodegradation in blends. Particularly, in PVA/OR-fiber blends (PStOR), degradation was much slower in crosslinked (PStORX) specimens. In both blends, about 50-80% mineralization was achieved within 30 days (Figure 6).

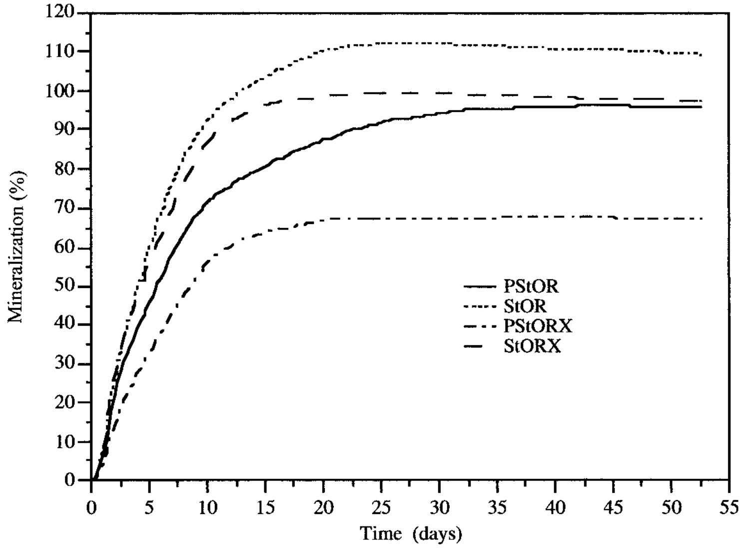

Figure 6. Mineralization of PStOR, StOR, PStORX and StORX

Conclusion

The thermal stability of PVA was appreciably greater than that of OR fibers as expected from their respective chemical structures. However, compared to neat PVA, only a modest decrease of the decomposition temperature was observed when PVA and OR-fibers were blended together, indicating potential usefulness of such blends in thermoplastic applications. The water permeability properties and biodegradability of hybrid films in compost environment yielded promising results. Particularly, water retention and the sustained integrity of films during water permeation was significant in spite of the hydrophilic nature of PVA, starch and OR. The addition of a crosslinking agent to the formulations affected the extent of degradation. High mineralization values were observed in a relatively short time and significantly higher biodegradation was observed in PVA containing Starch-OR-fiber blends. A possible stimulating effect of lingocellulosic fillers on the biodegradation of PVA in blends is being investigated.

Acknowledgements

Research was done as collaboration between the University of Pisa, Italy and the Plant Polymer Research Unit of the ARS-USDA, National Center for Agricultural Utilization Research, Peoria, Illinois. The authors thank Ms. Paulette Smith, Ms. Jan. Lawton and Mr. Gary Grose for technical assistance. The financial support for Ms. Patrizia Cinelli's Ph.D. thesis research was provided by the Ministry of University and Technology of Italy and in part by the NCAUR/ARS/USDA. We are grateful to Sunflo Citrus Limited, Pakistan for providing gratis orange by-products materials used in this study. Assistance of the USDA International Program Office is greatly appreciated.
The financial support by MIUR CoFin 2000 project is also acknowledged.

[1] Mc. Cormick, C. L.,"Agricultural Applications" Chapter in: Encyclopedia of Polymer Science and Engineering, Vol. 1, 2nd Ed., John Wilet & Sons, NY, 1984, p.611.
[2] E. Chiellini, P. Cinelli, S. D'Antone, V.I. Ilieva, *Polymery*, **2002**, 47, 21.
[3] G. Scott, *Polym.Deg.Stab.*, **2001**, 68, 1.
[4] "Polymers from Agricultural Coproducts" Eds. Fishman M.L., Friedman R., Huang S.J. *ACS Symp. Ser.* 575, Washington DC, 1994.
[5] "Chemical and Materials from Renewable Resources" Eds. J.J. Bozell, ACS Symp.Ser. 784, Washington D, 2001.
[6] R.A.Young, Lignocellulosics-Plastics Composites, 1997, Sao Paolo Brazil, Ed. A.L. Leao, F.X .Carvalho, E. Frollini, p.1.
[7] E. Chiellini, P.Cinelli, L., .H. Imam, L. Mao. *Biomacromolecules*, **2001**, 2, 1029.
[8] S. M, Lahalih, S. A. Akashah, F. H., Al-Hajjar, *Ind.Eng.Chem.Res.* **1987**, 26, 2366.
[9] R.Coffin, M.L. Fishman, T.V. Ly, *J.Appl.Polym.Sci.* **1996**, 57, 71.
[10] E. Chiellini, P.Cinelli, E. Grillo Fernandes, E. R. Kenawy, and A. Lazzeri, *Biomacromolecules* **2001**, 2, 806.
[11] E. Chiellini, P.Cinelli, S.H. Imam, L. Mao, In: *Biorelated Polymers-Sustainable Polymer Science and Technology*, E. Chiellini, H. Gil, G. Braunegg, J. Buchert, P. Gatenholm, and M. Van der Zee (eds.), Kluwer Academic/Plenum Publishers, pp. 87-100.
[12] L.R. Krupp, W.J. Jewell, Environm.Sci.Technol. **1992**, 26, 193
[13] L. Chen, S. H. Imam, S. H. Gordon, R.V. Greene, J Environ Polym Degr **1997**; 5 (2): 111-117.
[14] E. R Kenawy. P. Cinelli, A. Corti, S. Miertus, E. Chiellini *Macromol. Symp.* **1999**, 144, 351
[15] Chiellini E., Cinelli P., Corti A., Kenawy E.R., Grillo F. E., Solaro R. *Macromol. Symp.* **2000**, 152, 83.

[16] Chiellini E., Cinelli P., Corti A., and Kenawy E.L. *Polym.Degrad Stab.* **2001**, 73, 549
[17] Chiellini E, Corti A, Solaro R. Polym Degrad Stab 1999; 64 (2): 305-312.
[18] S. Matsumura, N. Tomizawa, A. Toki, K. Nishikawa, K. Toshima, *Macromolecules* **1999**, 32, 7753
[19] H. Sawada In Doi Y, Fukuda K, editors. Biodegradable Plastics and Polymers, Amsterdam: Elsevier, **1994**. p. 298.
[20] N.E. Sharabi, R. Bartha *Environ. Microbial.* **1993**, 59, 1201
[21] J. Shen, R. Bartha *Appl. Environ. Microbial.* **1996**, 62, 1428