Polymer Blends of Steam-Explosion Lignin and Poly(ε-caprolactone) by High-Energy Ball Milling

Rachele Pucciariello,[1] Carlo Bonini,[1] Maurizio D'Auria,[1] Vincenzo Villani,[1] Gaetano Giammarino,[1] Giuliana Gorrasi[2]

[1]Dipartimento di Chimica, Università della Basilicata, Via Nazazio Sauro 85, 85100 Potenza, Italy
[2]Dipartimento di Chimica ed Ingegneria Alimentare, Università di Salerno, Via Ponte Don Melillo, Fisciano Salerno, Italy

ABSTRACT: Lignin powder, obtained from an abundant and low-cost source, straw, through a low-environmental-impact process, steam explosion, was used for the preparation of blends with a biodegradable polyester, poly(ε-caprolactone) (PCL), with an innovative technique, high-energy ball milling. Lignin strongly stabilized PCL against UV radiation. The modulus of the blends increased with the addition of lignin; nevertheless, the elongation at breaking decreased. Through thermal characterization (differential scanning calorimetry and dynamic mechanical analysis), lignin and PCL were found to be immiscible. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 309–313, 2008

Key words: biodegradable; blends; polyesters; renewable sources

INTRODUCTION

Lignin is a natural amorphous polymer, which together with cellulose and hemicellulose, is one of the main constituents of wood. It is generally obtained as a byproduct in paper production through separation from cellulose fibers. Its structure depends of the kind of process used for delignification.[1]

The separation of lignin from cellulose is done by means of the pulping process in the paper industry, which presents environmental problems and gives altered lignin. Nowadays, new delignification processes, in particular, the steam explosion process, exist that have been largely developed because of the environmental problems related to the pulping process and that allow one to obtain a less altered lignin.

Lignin obtained by the steam explosion process has very rarely been used to obtain new materials. Few articles are present in the literature about this. More than 20 years ago, an article[2] was published about the use of steam-exploded wood lignin as an extender in asphalts. More recently, Meister et al.[3] used lignin from steam-exploded wood to obtain graft copolymers of lignin with styrene. Last,[4–6] softwood lignin from steam explosion was used in conjunction with different plastics to prepare binderless composites. These studies all used the steam explosion process to obtain lignin from wood. Nevertheless, another important source of lignin exists, straw, a very diffuse and very low-cost agricultural residue. In the recent past, we investigated the possibility of using steam exploded lignin from straw to prepare blends with largely diffuse synthetic polymers, such as different-grade polyethylenes and polystyrenes.[7]

Nevertheless, although synthetic polymers have produced hardly overvaluable benefits for recent life, the environmental impact of nonbiodegradable plastics, especially when used for disposable objects, is becoming enormous. Moreover, petroleum resources are limited and will be available at a low price for a finite time. Therefore, the development of biodegradable materials and/or materials from renewable sources, such as polyesters, polylactides, and polysaccharides, especially for brief packaging and disposable products, is becoming more and more urgent. Nevertheless, such polymers show, in general, poor mechanical, thermal, and barrier properties, which prevent their large commercial diffusion.

Poly(ε-caprolactone) (PCL) is a quality biodegradable polymer, which makes it attractive for a series of applications, including disposable food service items, food packaging, health care products, and agricultural films.[8] In the last few years, interest in PCL has strongly increased because of rapidly increasing environmental concerns. Nevertheless, like most biodegradable polymers, PCL suffers the typical problems discussed previously.

In this study, we used straw lignin, largely present in our region because of the large abundance of agricultural crops, separated through the steam explo-

---

WILEY
InterScience®
DISCOVER SOMETHING GREAT

sion process, developed at Enea of Trisaia (Matera, Italy), to obtain blends with PCL with a new alternative method for the preparation of blends based on solid-state mixing at room temperature, which involves the efficient mixing of two or more species by mechanical milling, called *high-energy ball milling* (HEBM).[9] It consists of repeated events of energy transfer, promoted by the milling device, from the milling tools (generally balls) to the milled powder. During milling, the powder particles crack, clean surfaces are produced, and atom diffusion and intimate mixing are promoted. As a result of the prolonged milling action, when the energy transferred during the hit is enough to overcome the activation barrier, chemical reactions may occur. Recently, it has been proven that HEBM of polymeric materials can help one to obtain materials with new characteristics that are difficult to obtain with other conventional processes.[10,11] Although mechanical action can have deleterious effects on solid polymers through the breaking of chains and the creation of free radicals, the selection of opportune milling conditions in HEBM can be successfully used to produce polymeric blends with increased mechanical properties.[10–12]

This study was a first step in the production of low-cost materials, with potential applications in the fields of packaging, health care products, agricultural films, and disposable objects, to find new applications for lignin, a naturally abundant and low-cost polymer, for which, nowadays, only a small market exists.

EXPERIMENTAL

Materials

Lignin was obtained from straw through the steam explosion process, performed at Enea [Trisaia (Matera), Italy]. Its weight-average molecular weight (M_w) was evaluated by gel permeation chromatography as $M_w = 3000$.

PCL (Capa 6501, $M_w = 50,000$) was kindly supplied in powder form by Solvay.

Blend preparation

Powders of lignin and PCL were milled in the solid state in a Retsch GmbH (Germany) centrifugal ball mill (model S 100). Sample masses were milled in a 50-cm^3 cylindrical steel jar with five steel balls 10 mm in diameter. The rotation speed used was 580 rpm, and the milling time was fixed at 40 min. The PCL/lignin mixtures and the pure milled PCL were molded in a hot press (Carver, Inc.) at 100°C. In all cases, films 250 ± 50 μm thick were formed; they were rapidly quenched in a water–ice bath (0°C).

TABLE I
Samples Used Throughout This Study

Sample	Lignin content (wt %)
PCL	0
PCL1	1
PCL3	3
PCL10	10
PCL20	20
PCL30	30
PCL40	40

In Table I, all the samples with the codes used to identify them are indicated. The blend composition is expressed as the weight percentage of lignin (e.g., PC30 had 30 wt % lignin).

Material characterization

Thermal analyses of the samples reported in Table I were carried out with a differential scanning calorimeter (DSC7, PerkinElmer), and the samples were heated from −100 to 200°C at 20°C/min, with liquid nitrogen as a coolant and purging helium inside the cell. Data were analyzed through Pyris 1 software, running under Windows NT 4.0. As usually, the melting temperatures were taken as the maxima of the corresponding endothermic peaks, and the glass-transition temperatures were taken as those corresponding to the point where half of the increase of the heat capacity occurred. The error was ±0.5°C. The apparatus was calibrated with the melting temperatures of indium and zinc and the heat of fusion of indium. Before each experiment, the baseline in the range of interest was optimized; then, it was subtracted from the corresponding calorimetric curves.

Dynamic mechanical thermal analyses were performed with a DMA Q800 analyzer (TA Instruments, New Castle, DE), and the data were analyzed through TA5000 Advantage Software Suite. The measurements were carried out with liquid nitrogen as a coolant to allow scansions from −150 to 40°C. The scanning rate was 5°C/min during the application of forced oscillations with a frequency of 1 Hz in the 1-point bending mode.

The mechanical properties of the samples were evaluated from stress–strain curves obtained with a dynamometric apparatus (Instron 4301, Waltham, MA). The experiments were conducted at room temperature with a deformation rate of 10 mm/min. Elastic moduli were derived from the linear part of the stress–strain curves, which gave the sample a deformation of 0.1%.

The photodegradation of the neat polymers and the blends was investigated. Before the measurements, the samples were acetylated. The lignin sample (ca. 100 mg) was acetylated with 2 mL of acetic

anhydride/pyridine (1 : 1, v/v) at room temperature overnight in a 50-mL flask. Ethanol (25 mL) was added, and after 30 min, the solvents were removed by film evaporation. Repeated addition and removal (film evaporation) of ethanol (10 times) resulted in the removal of acetic acid and pyridine from the sample. The acetate was dried *in vacuo* over KOH and P_2O_5.

The samples were irradiated for 48 h by a 15-W UV lamp and were then analyzed by gel permeation chromatography on a Hewlett-Packard 1100 HPLC with a H-P Plgel 5 μ Mixed-C column (Agilent Technologies, Foster City, CA). Tetrahydrofuran was used as the mobile phase. Spectrophotometric-grade tetrahydrofuran was used and distilled (over $LiAlH_4$) before use. The chromatograms were obtained with a UV detector (diode array) at 280 nm. The conversion from elution time to molecular weight was performed with calibration obtained with polystyrene samples.

RESULTS AND DISCUSSION

Tensile tests were performed to study the effect of lignin on the basic mechanical properties of the PCL.
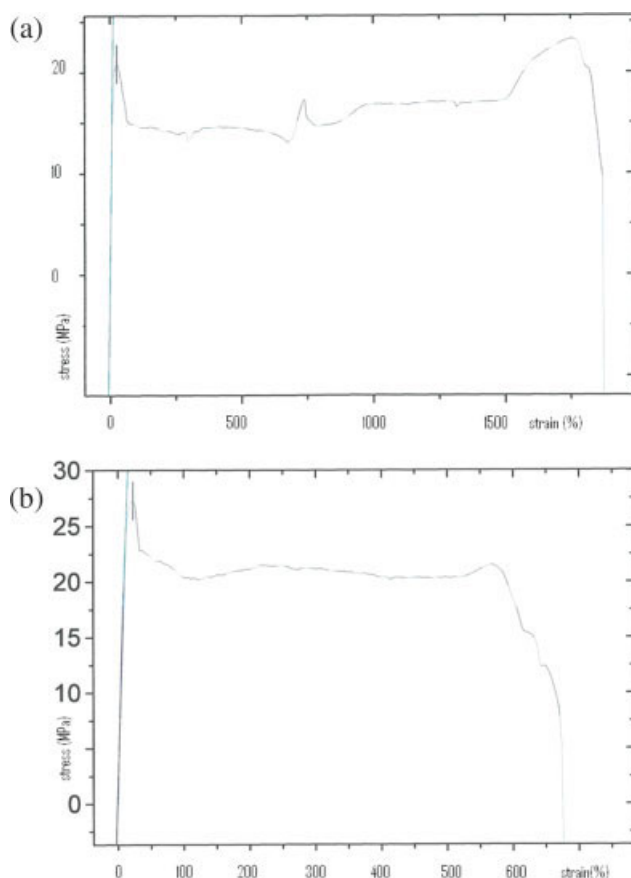

Figure 1 Stress–strain curves for neat (a) PCL and (b) PCL1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Mechanical Parameters Evaluated from the Stress–Strain Curves

Sample	E (MPa)	σ_y (MPa)	σ_b (MPa)	ε_b (%)
PCL	200	20.8	9.5	1870
PCL1	194	27.3	2.5	674
PCL3	197	26.5	0.1	342
PCL10	268	8.5	0.15	227
PCL20	317	10.2	4.3	80
PCL30	509	13.9	12.5	21
PCL40	512	11.1	7.3	7

E = Young's modulus; σ_y = stress at yielding; σ_b = stress at breaking; ε_b = strain at breaking.

In Figure 1, we report the stress–strain curve for neat PCL as a reference and for PCL1 as an example.

In both cases, the typical curve of thermoplastic materials was observed, with a first linear region, from whose slope the Young's modulus was calculated, followed by the maximum, corresponding to the yield point. Then, a plateau region was recorded, where the strain remained about constant upon deformation. Last, a sudden increase in the strain took place, followed by specimen breaking.

In Table II, for all of the samples, the values of the mechanical parameters evaluated in the tensile tests are reported.

The Young's modulus increased with increasing lignin content in the sample. As far as the other mechanical parameters are concerned, the stress at breaking increased with respect to the pure polymer up to 3 wt % lignin in the sample. In contrast, the other mechanical properties decreased with lignin addition, in particular, the elongation at break.

Similar results were reported in the literature for nonpolar thermoplastics and lignin blends[3,4] and, more generally, for polymer composites, in which poor compatibility took place between the two components.

To evaluate the compatibility between lignin and PCL, differential scanning calorimetry scans were performed. The thermal properties are reported in Table III. The values of the transition temperatures appeared the same in the blends and in the neat components, which pointed to the immiscibility of the blends.

The dynamic mechanical properties, namely, the storage component of the modulus and the loss factor were evaluated for the neat polymer and for two representative blends, that is, PCL10 and PCL30. In Figure 2(a), we report the storage modulus as a function of the temperature in the temperature range −100 to 40°C. For pure PCL, we observed an almost constant value of the elastic modulus up to −60°C, followed by an evident drop associated with the

TABLE III
Melting Temperatures (T_m's) of PCL and the Glass-Transition
Temperatures of PCL (T_{g1}'s) and Lignin (T_{g2}'s)

Sample	T_{g1} (°C)[a]	T_m (°C)[a]	T_c (°C)[a]	T_{g2} (°C)[a]	T_{g1} (°C)[b]	T_{g1} (°C)[c]
PCL	−55	55	32		−39	−61
PCL1	−54	56	34	138		
PCL3	−55	56	34	136		
PCL5	−55	55	33	134		
PCL10	−55	55	33	138	−41	−61
PCL20	−55	55	33	133		
PCL30	−55	55	34	136	−40	−53
PCL40	−55					

T_c = crystallization temperature.
[a] Evaluated by differential scanning calorimetry.
[b] Evaluated by dynamic mechanical analysis (maximum of tan δ).
[c] Evaluated by dynamic mechanical analysis (storage modulus drop).

glass transition of PCL. After the transition, the modulus showed an almost linear decrease with temperature up to 40°C. The moduli of PCL10 and PCL30 were higher than that of neat PCL in the whole investigated temperature range, and the increment was higher with increasing lignin content in the sample. In particular, for PCL and PCL10, the

storage modulus constantly decreased with increasing temperature. In contrast, for PCL30, after the drop at about −60°C, it remained about constant. This sample behaved as a hard material. The storage modulus, in the whole interval of temperature, was much higher than that of the other samples and, in particular, higher than that of PCL.

The increase in the modulus for PCL10 and PCL30 with respect to neat PCL was about 30 and 116%, respectively, at −90°C; 130 and 490%, respectively, at 0°C; and 125 and 500%, respectively, at 30°C.

We could explain the trend of the enhancement of the modulus as a function of the temperature by taking into account that above the glass-transition temperature, when the materials became soft, the reinforcement effect of the lignin particles became prominent because of the restricted movements of
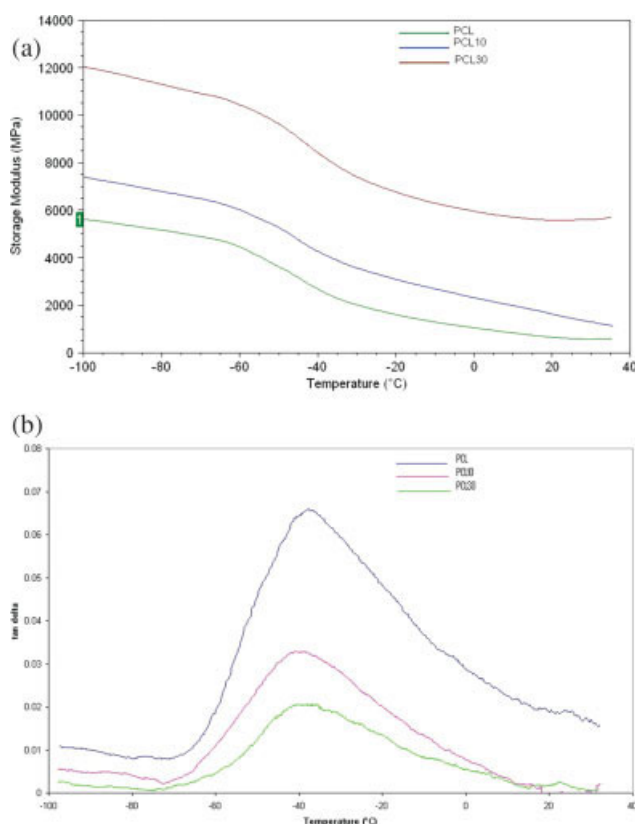

Figure 2 Storage component of the (a) modulus and (b) loss factor (tan δ) as a function of temperature for PCL, PCL10, and PCL30. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
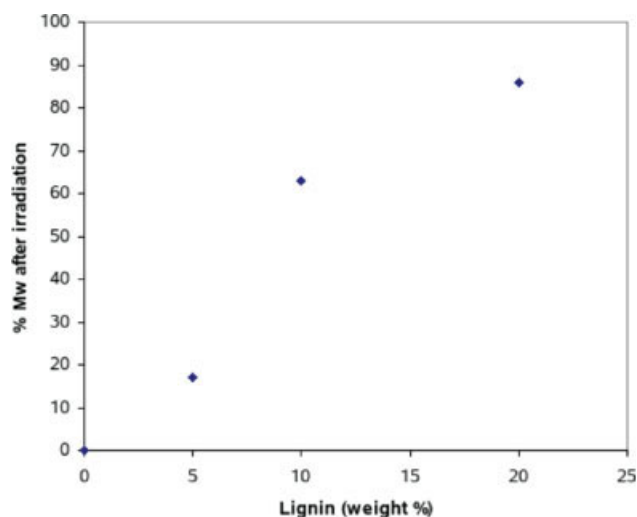

Figure 3 Percentage average molecular weight hold after irradiation of the lignin-PCL blends with a 15-W UV lamp for 48 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the polymer chains. In fact, the confinement of the polymer chains increased the viscosity and the mechanical properties of the system significantly. This behavior was attributed to both mechanical reinforcement by lignin particles and extended intercalation of the PCL chains, especially at the higher temperatures. In Figure 2(b), the trend of tan δ is reported for three samples in the same temperature range. The intensity of the signal strongly decreased with increasing the lignin content in the sample. The decrease was too large to be only attributable to the lower content of PCL in the blends, but it was likely due to the reduced mobility of the PCL chains in the presence of more and more lignin particles.

The samples were tested for the UV stability determination of the effect of lignin presence and content. The results of photodegradation are reported in Figure 3. The addition of lignin caused a minor decrease in the average molecular weight after irradiation with increasing the content of lignin, which suggested a protective action against photooxidation exerted by the filler.

The decrement of the stress and the elongation at break of the considered blends were ascribed to the poor miscibility between lignin and PCL. In these systems, rigidity is ordinarily improved, but strength, elongation, and toughness are sacrificed. In fact, as was also true in our case, as far as the modulus is concerned, it generally increases after the addition of lignin. This result would suggest that lignin may be used as a reinforcing agent, that is, as a filler suitable for increasing such mechanical features of the material as general rigidity but also the dimensional stability and the shrinkage. In general, inorganic fillers are used to this aim, but the lignin low abrasivity, low cost, and absence of toxicity could render it competitive with these materials.

In our opinion, these properties may be increased through the use of a compatibilizing agent between PCL and lignin.

The photodegradation behavior clearly showed that the neat polymer was strongly degraded by UV radiation, whereas in the lignin-containing blends, we observed a much lower degradation, which strongly decreased with increasing lignin content; this indicated an antioxidant action by the lignin. The UV stabilization performed by lignin was due to the presence of phenolic groups, which made the lignin act as a radical scavenger, which inhibited or slowed the radical processes of degradation.

CONCLUSIONS

Biomass has enormous potential as a source of new and interesting polymeric materials in a wide range of applications. Nevertheless, until now, only a small number of research groups have been involved in such activities. In the Basilicata region (Italy), agricultural residues, for example, straw, are largely present; these represent a particularly low-cost lignin source. Moreover, in the same region, Enea uses a particularly efficient and low-environmental-impact method (steam explosion) to separate lignin from cellulose and hemicellulose.

In this study, we used straw lignin, produced by Enea, blended with the biodegradable polyester, PCL. The blends were prepared with the innovative technique of HEBM. Lignin stabilized PCL against UV radiation. As far as the mechanical properties were concerned, the addition of lignin increased the modulus of the blends with respect to the neat polymers. Nevertheless, the presence of lignin decreased the tensile strength and the elongation at break. These results were related to the poor compatibility between lignin and the synthetic polymer and may be overcome with a compatibilizing agent. This is the subject of a work in progress.

References

1. Glasser, W. G.; Sarkanen. S. Lignin: Properties and Materials; ACS Symposium Series 398; American Chemical Society: Washington, DC, 1989.
2. Sunstrom, D.; Kiel, H. E.; Daubenspack, T. H. Ind Eng Chem Prod Res 1983, 22, 496.
3. Meister, J. J.; Chien, M. Macromolecules 1991, 24, 6843.
4. Angles, M. N.; Regnant, J.; Montane, D.; Ferrando, F.; Farriol, X.; Salvado, J. J Appl Polym Sci 1999, 73, 2485.
5. Angles, M. N.; Ferrando, F.; Farriol, X. J Salvado Biomass Bioenergy 2001, 21, 24.
6. Velasquez, J. A.; Ferrando, F. J Salvado Ind Crops Prod 2003, 18, 17.
7. Pucciariello, R.; Villani, V.; Bonini, C.; D'Auria, M.; Vetere, T. Polymer 2004, 45, 4159.
8. Biodegradable Polymers and Plastics; Vert, M.; Fejen, J.; Albertsson, A. C.; Scott, G.; Chiellini, E., Eds.; Royal Society of Chemistry: London, 1992.
9. Rowlands, S. A.; Hall, A. K.; Mc Cormick, P. G.; Street, R.; Hart, R. J.; Ebell, G. F.; Donecker, P. Nature 1994, 22, 367.
10. Shaw, W. J. D. Mater Sci Forum 1998, 19, 269.
11. Magini, M.; Burgio, N.; Iasonna, A.; Martelli, S.; Padella, F.; Paradiso, E. J Mater Synth Proc 1993, 3, 1.
12. Sorrentino, A.; Gorrasi, G.; Tortora, M.; Vittoria, V.; Constantino, U.; Marmottini, F.; Padella, F. Polymer 2005, 46, 1601.