

# Preparation, Physico-chemical Characterization, and Optical Analysis of Polyvinyl Alcohol-Based Films Suitable for Protected Cultivation

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**ABSTRACT:** The use of biodegradable polymer films for mulching is a topic of great interest both from the environmental point of view and for the intrinsic properties that the above films, when appropriately designed, might have. In the present article we report on a synthetic approach that, starting from existing biodegradable polymers, leads to a new material characterized by a time-controlled biodegradation. The idea that subsides is to bridge polyvinyl alcohol (PVOH) chains through polycaprolactone (PCL) crosslinks. In such a way, PVOH loses its water sensitivity and can stand on the ground for the time needed for the mulching to occur, while the PCL crosslinks, being sensitive to (slow) fungal attack, will undergo cleavage, followed by the complete bio-assimilation of the re-

sidual PVOH chains. The number of crosslinks introduced can control time of biodegradation. The polymers are characterized in their intrinsic chemical-physical properties, while a preliminary evaluation of their efficiency as mulches is obtained through the analysis of their thermal behavior when deposited on an irrigated soil. The results are also compared with a model approach able to predict the thermal behavior of a film in specific environmental conditions. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 622–632, 2002

**Key words:** blending; biodegradable; UV-Vis spectroscopy; modeling

## INTRODUCTION

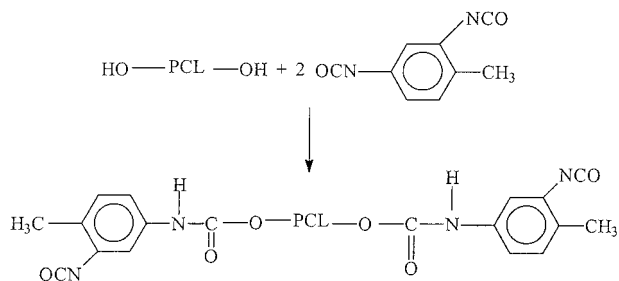
The use of plastic films for coverage in agriculture dates back to the 1960s. At that time, plastics had an essentially mechanical role, to protect cultivation from injuries from the weather. More and more, their role has become active, as to reduce water and mineral losses, to filtrate solar radiation to minimize wavelengths sensitive to pathogens and to maximize wavelengths sensitive plants growth factors, to improve solar energy utilization for soil sterilization, and in doing so reducing the need for chemicals (such as methyl bromide).<sup>1–4</sup> The results of this, the increase of plastic usage in agriculture, has been dramatic, and is now at about 3 million tons per year, 50% of which is for protection of cultivation. Most films belong to the family of polyolefins and their copolymers, like poly(ethylene-co-vinyl acetate) (EVA), monolayer, or coextruded multilayers, with a minimal, and still reducing, amount of poly(vinyl chloride) (PVC) for mulching or ensilage.<sup>5</sup> The amount of plastics at the end of their

useful lifetime poses serious problems for their disposal, due to restrictions to land filling or incineration, and difficult recycling for their state of photo oxidation, dust, and organic matter deposition, even severe poisoning for chemicals and pesticides.<sup>6</sup> We have, in recent years, directed our research on biodegradable polymers to be proposed in agriculture in substitution of classical nonbiodegradable plastics.<sup>7</sup> These materials have originally been developed for the packaging industry. Starch-based blends, aliphatic polyesters, vinyl alcohol polymers are the most successful examples.<sup>8</sup> In many countries, even though their price is normally higher than biophobic plastics, they have found commercial acceptance, due either to a favorable legislation or to the increased eco-sensitivity of customers.

To be applied in agriculture, it is necessary to tailor their mechanical properties, optical behavior, and biodegradation time according to the different specific usage, i.e., in the open field or under tunnels, in summer or winter climates, just to mention two most important variables.<sup>9</sup>

In the present article we report on the spectroscopic, thermal, and optical analysis of innovative biodegradable film made of polyvinyl alcohol and polycaprolactone. Moreover, their microscopic appearance before and after their exposure to conditions typical of protected cultivation have been investigated.

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Scheme 1 Functionalization of PCL.

## EXPERIMENTAL

### Materials

Polyvinyl alcohol (PVOH) is supplied from Idroplast, Italy. It is a film grade formulation characterized by 96% hydrolysis of the original polyvinyl acetate precursor of high molecular weight (>100,000). It is soluble in water at moderate temperature (40–50°C).

Polycaprolactone (PCL) is supplied pure from Solvay Interox. It has an  $M_w = 530$  a.m.u., and is hydroxyl terminated.

Toluen-2, 4-diisocyanate (TDI), 98% pure, supplied by Fluka, is used without further purification.

All solvents were purified according to standard procedures.

### Preparation of PCL(NCO)<sub>2</sub>

In a glass reactor fitted with a nitrogen inlet and a reflux condenser, 1 g of PCL (1.9 mmol) was charged and dissolved in 10 mL of chloroform; 0.66 g of TDI (3.8 mmol), previously dissolved in a minimum amount of chloroform, was added dropwise through a separatory funnel.

The reaction was carried out for 3 h at reflux, then stopped by cooling down the solution at room temperature. Solvent was removed by vacuum stripping at moderate temperature (>50°C) and a viscous fluid amber-like was obtained. It was washed three times with petroleum ether, then was characterized by infrared spectroscopy. The occurrence of the reaction was checked by the formation of the urethane bond at 1560  $\text{cm}^{-1}$ , together with the presence of the residual isocyanate at 2270  $\text{cm}^{-1}$ .

### Reaction between PVOH and PCL(NCO)<sub>2</sub>

In the preparation of PVOH-PCL 1/100, 5 g of PVOH (0.11 mol of repeating units) were dissolved in 100 mL of a 1/1 mixture of dimethylsulfoxide/dimethylacetamide (DMSO/DMAc). To this solution 1 g of PCL(NCO)<sub>2</sub> (corresponding to 1 PCL graft per 100 repeating units of the PVOH chain) previously dissolved in 10 mL of DMSO/DMAc, were added. The solution was taken at 100°C for 2 h, then it was cast on

a glass plate using a Gardner film applicator and the solvent was evaporated at 150°C until dry. Finally, a postcure step of 1 h at 180°C was found necessary for the reaction completion.

On the final film, about 50  $\mu\text{m}$  thickness, the absence of isocyanate was checked at FTIR, by the disappearance of the N=C=O stretching vibration at 2270  $\text{cm}^{-1}$ .

### Techniques

FTIR analysis was performed on the films mounted on an infrared film holder with a Perkin-Elmer spectrometer model Paragon 500 at a resolution of 2  $\text{cm}^{-1}$  in the spectral range of 4000–400  $\text{cm}^{-1}$ .

Differential scanning calorimetry (DSC) was performed using a DSC Mettler TC11 in the temperature range from 25 to 250°C at 20°C/min (I run) followed by rapid cooling (quenching) to –100°C and from –100 to 250°C at 20°C/min (II run).

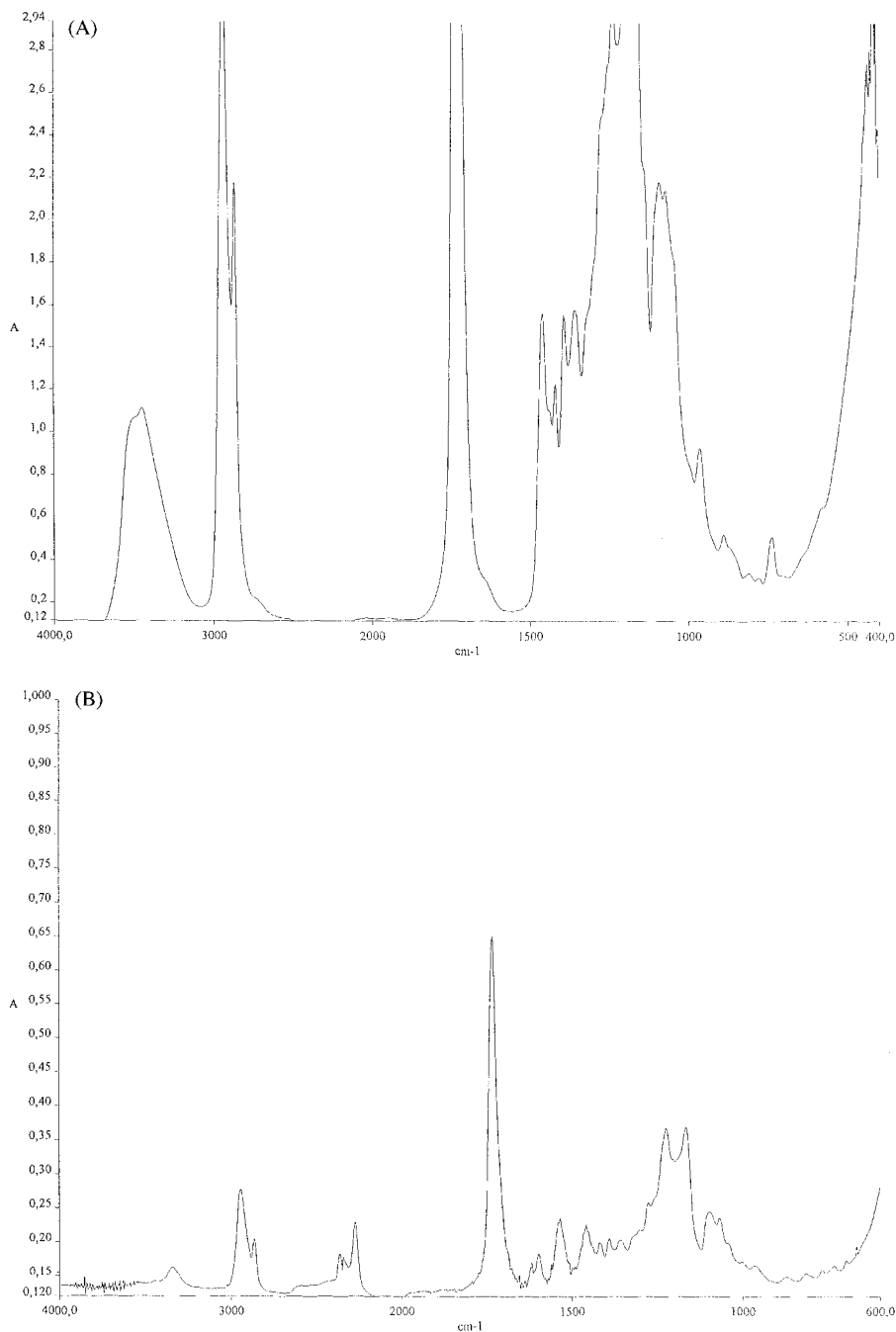
Scanning electron microscopy (SEM) was performed by using an SEM Philips model XL 20 on film surfaces coated with Au/Pd alloy.

Optical analysis was performed on the films by means of an optical bench particularly designed by JASCO. It consists of an integrated system comprising an UV/VIS/NIR Spectrophotometer model V-570 and an FTIR Spectrophotometer model 430. It allows the continuous scan of the specular and diffused transmittance and reflectance, together with the absorbance in the whole radiometric range from 190 to 12,500 nm for film thickness down to 0.020 mm; measurements can also be made at variable angles from perpendicular to 60°.

## RESULTS AND DISCUSSION

“Solarization” or “soil sterilization by plastics” is an agricultural practice where a continuous film is applied on a preirrigated soil during the hottest season for the time necessary to kill (or at least devitalized) all pathogens by means of the increase in temperature (normally 2 to 3 weeks).<sup>10</sup> The physical principle is the very high transparency of the film to incident solar radiation, and very high barrier of the same film to the thermal radiation coming out from the soil, particularly at wavelengths between 7 and 12  $\mu\text{m}$ . Other prerequisites of the film are a high barrier for gases (carbon dioxide, ethylene, and ammonia) produced by the soil microorganisms, and minimal thickness.

From previous studies, it was recognized that polyhydric macromolecules (like starch) or polyesters (like PET) have good solarization characteristics.<sup>7</sup> In our search for biodegradable films suitable for application or solarizing coverage, we have identified polyvinyl alcohol (PVOH) and polycaprolactone (PCL).<sup>11</sup> PVOH is a very good film forming plastic; it can be processed from solvents or from the melt, when in the presence of suitable plasticizers. It forms clear, tough films with



**Figure 1** Fourier transform infrared spectra of: (A) PCL; (B) PCL(NCO)<sub>2</sub>; (C) PCL 100.

a very high barrier to gases and also a strong absorbance in the thermal region. It is also biodegradable, the only purely C—C macromolecule that can be biodegraded.<sup>8</sup> Unfortunately, it has a very strong water sensitivity that impedes its use as solarizing film.

PCL is, on the contrary, insoluble in water, and it is reported to be compatible with PVOH.<sup>12</sup> In our study we have used PCL at a low molecular weight to bridge chemically different PVOH chains. By such a method, we can reduce the water sensitivity of PVOH so the film can stand on the soil surface for the time necessary to complete the solarization. Once the film has

been buried inside the same treated soil, anaerobic digestion of PCL bridges leaves uncrosslinked PVOH chains that will be dissolved by water and then biodegraded as well.

To impart chemical reactivity to PCL towards PVOH, hydroxyl-terminated PCL has been reacted with diisocyanates. In the present study 2,4-toluenediisocyanate has been used, but other diisocyanates, such as aliphatic or cycloaliphatics, can be used.

To study the influence of crosslink density on the water resistance, three different PVA-x-PCL polymers have been synthesized, having a PCL bridge every 25,

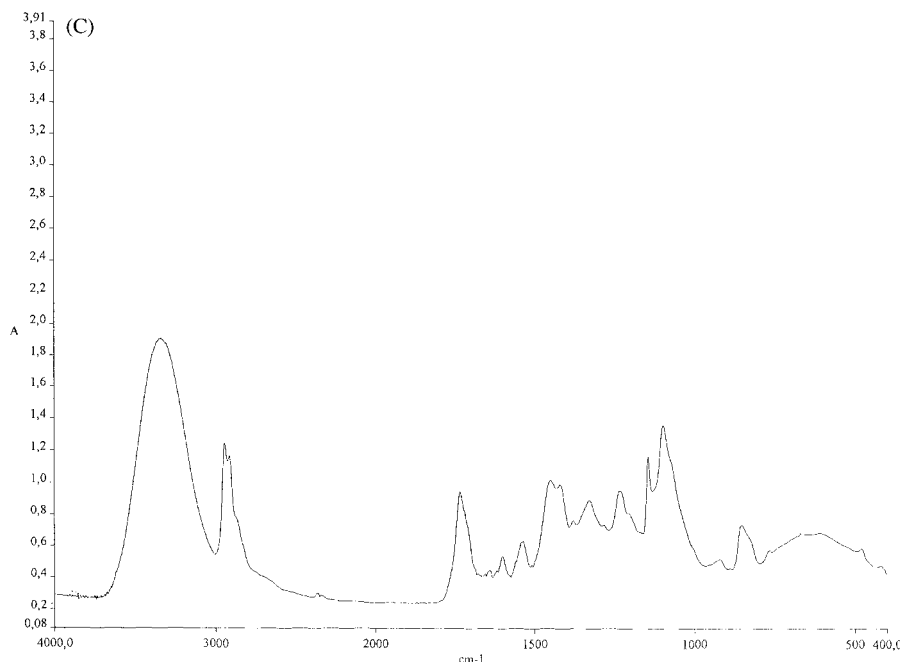


Figure 1 (Continued from the previous page)

50, and 100 repeating units of PVOH. The samples will be identified, through the paper, as PCL 25, PCL 50, and PCL 100.

The procedure for functionalization and crosslink is as follows: in a suitable solvent PCL is reacted at 80°C with a stoichiometric amount of TDI. The reactivity of the two isocyanate groups onto TDI is not the same, being that the isocyanate groups in the *para*-position is more reactive than that in the *orto*-position (Scheme 1).

The reaction is monitored by I.R., through the disappearance of the —OH stretching vibration of PCL and the appearance of the N=C=O vibration at 2270  $\text{cm}^{-1}$  [see Fig. 1(A) and (B)].

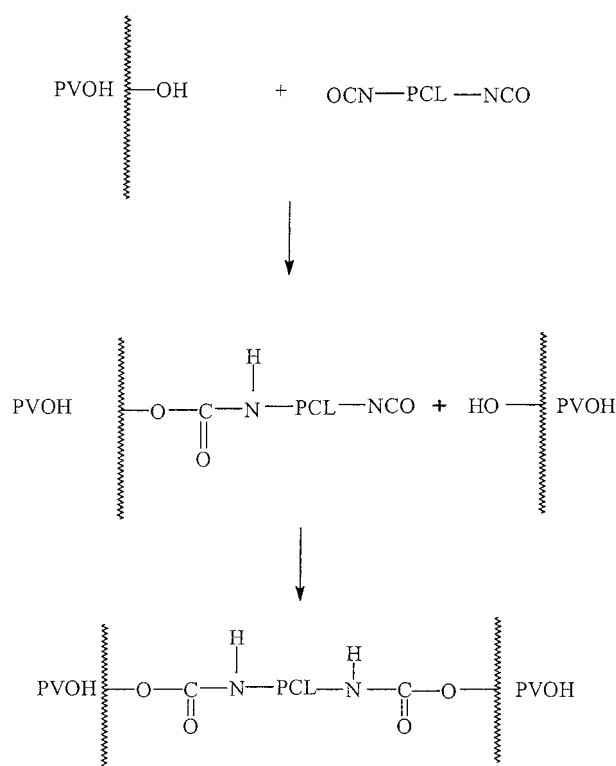
This polymer is still soluble. To it, a solution of PVOH was added in the chosen ratio. The overall concentration of the polymer was 4% by weight.

The solution was taken at 100°C for 2 h, then the viscous fluid was spread on a glass surface. The solvent was evaporated under vacuum at 100°C, then the film (50  $\mu\text{m}$  typical thickness) was cured at 180°C for 1 h. The reaction between PCL(NCO)<sub>2</sub> and PVOH was checked by the disappearance of the isocyanate at 2270  $\text{cm}^{-1}$  [see Fig. 1(B) and (C)]. The films are transparent and quite flexible (Scheme 2).

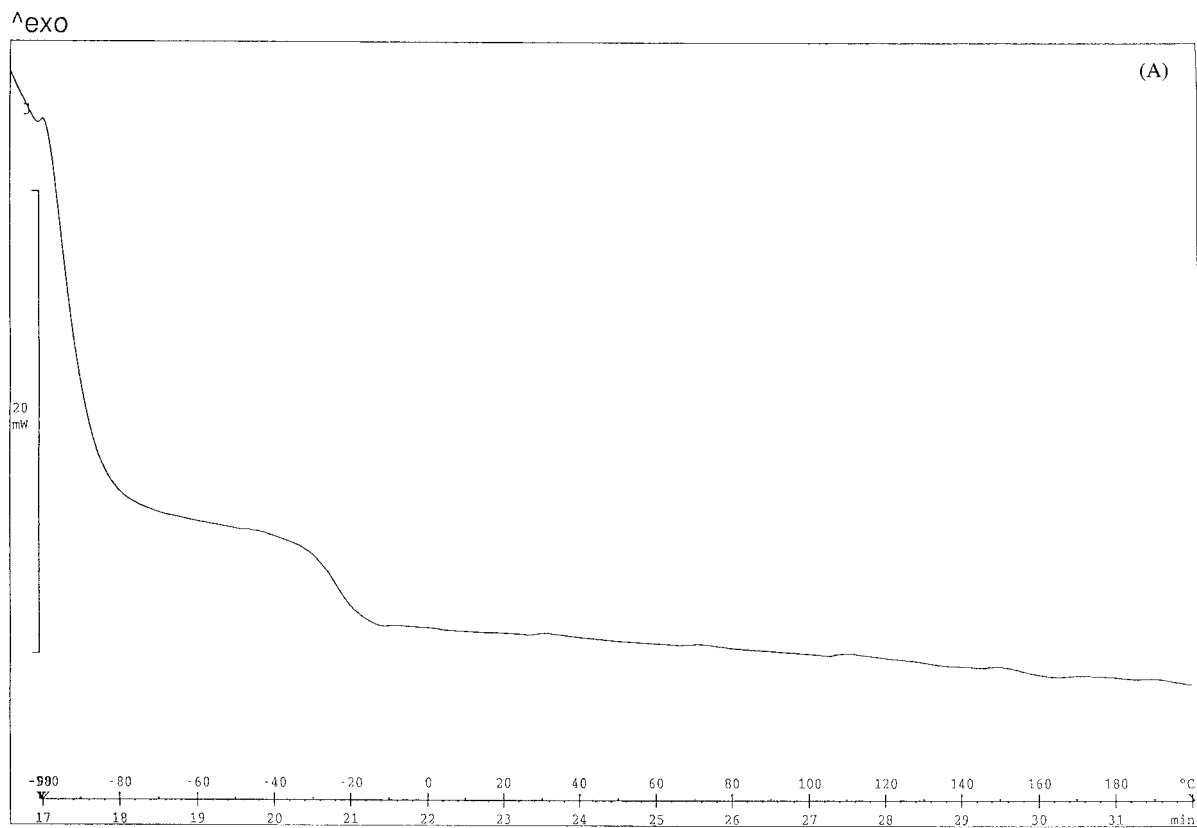
### Thermal analysis

In Figure 2 are reported the DSC traces (II RUN) of PCL(NCO)<sub>2</sub>, PVOH, and of the different PCL-x films. PVOH has a melting endotherm at 167°C and a glass transition at 70°C, while PCL melts at 45°C and has a  $T_g$  at -38°C. DSC traces of PCL 100 shows only the transition of PVOH, located at the same values of neat

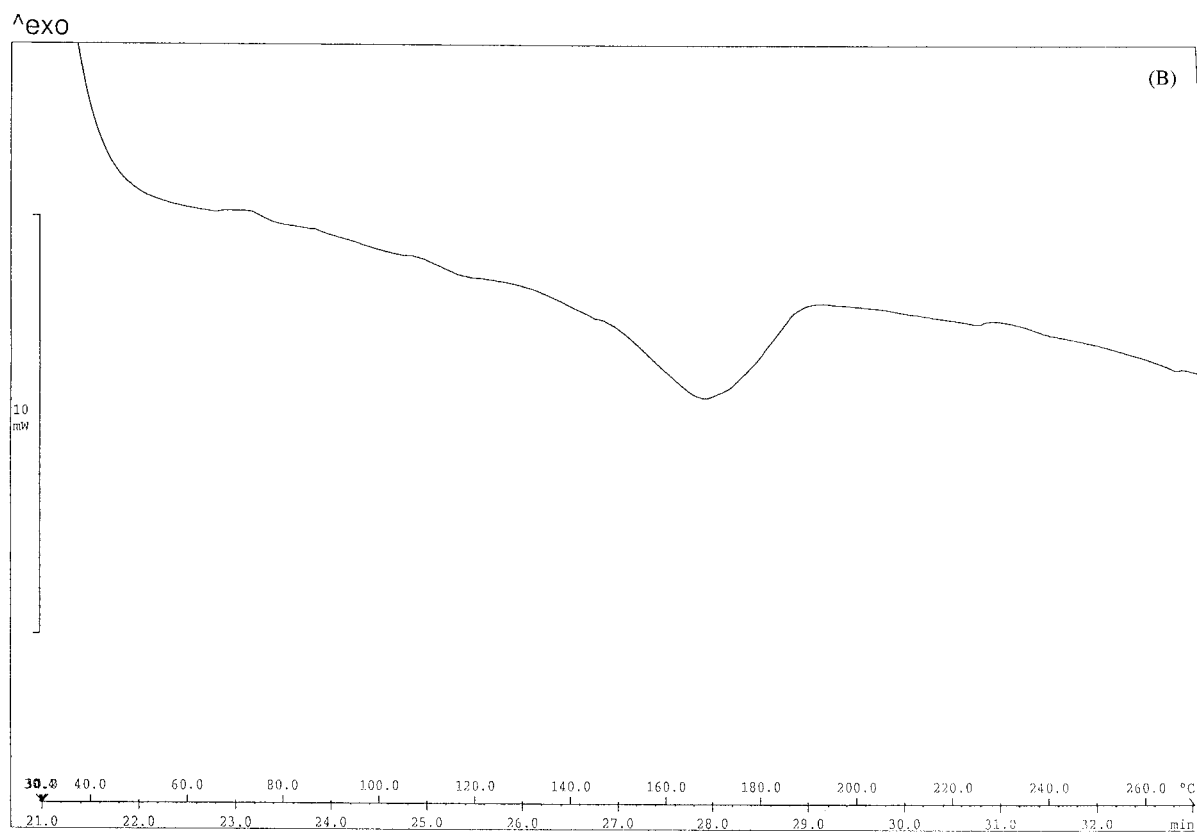
PVOH. Increasing the amount of PCL there is a broadening of the melting peak of PVOH and, for PCL 25, a new first-order transition occurs, peaking at about 100°C, superimposed to the  $T_g$  of PVOH, probably due to the melting of the PCL segments. The broadening of the PVOH melting is an indication that the crystalli-



Scheme 2 Reactions between PVOH and PCL(NCO)<sub>2</sub>.

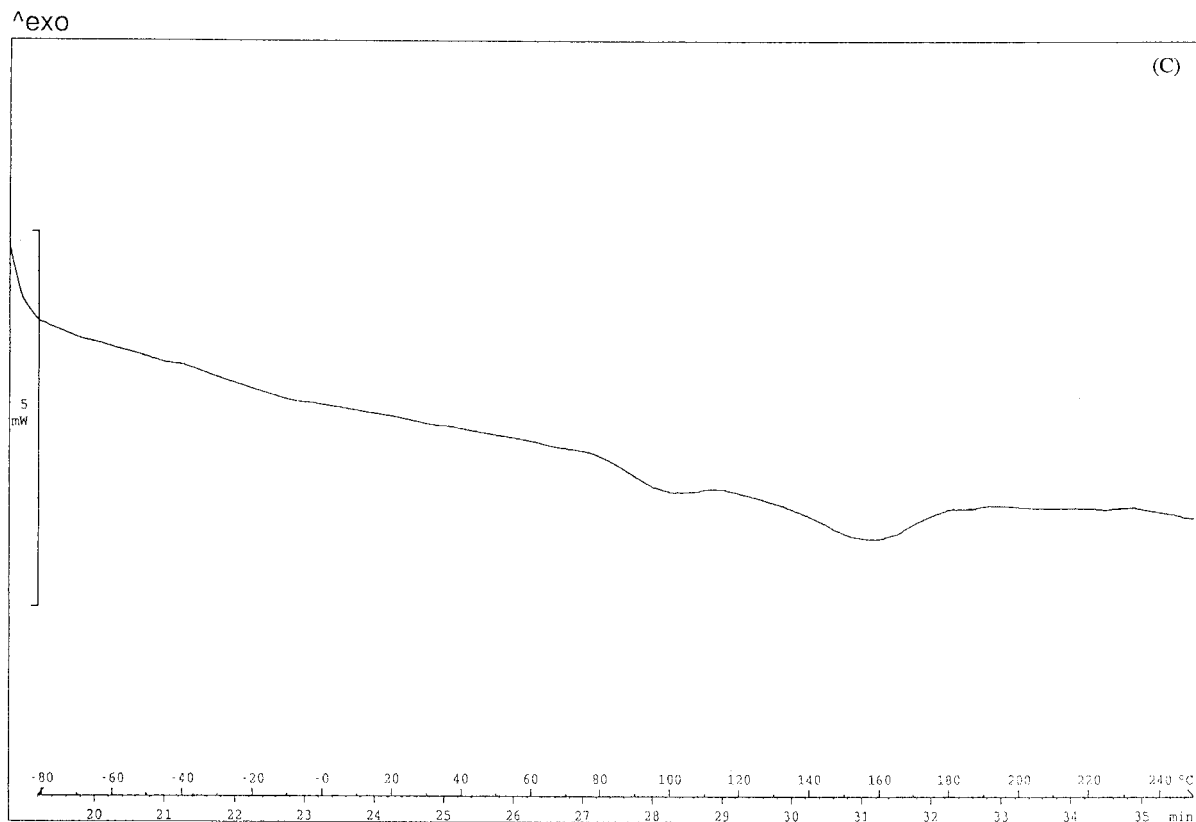


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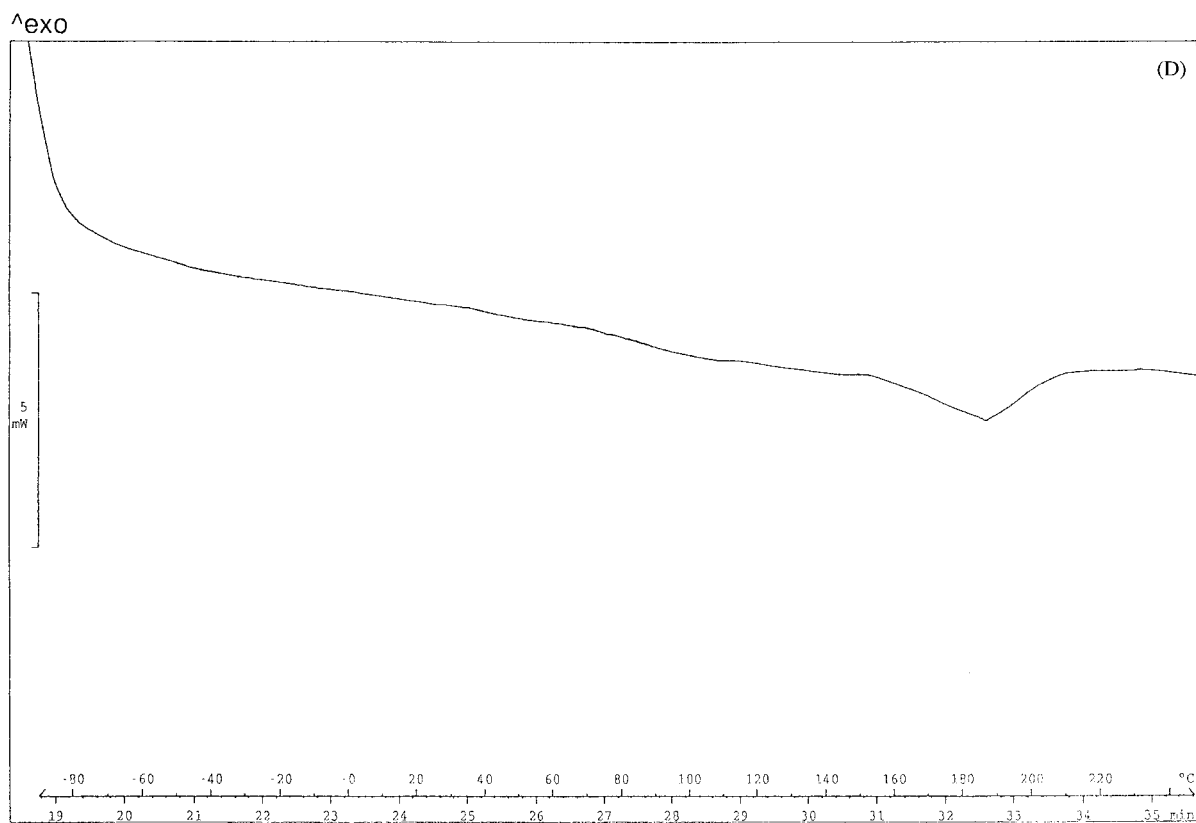


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Figure 2 Differential scanning calorimetry of: (A) PCL(NCO)<sub>2</sub>; (B) PVOH; (C) PCL 25; (D) PCL 50; (E) PCL 100.



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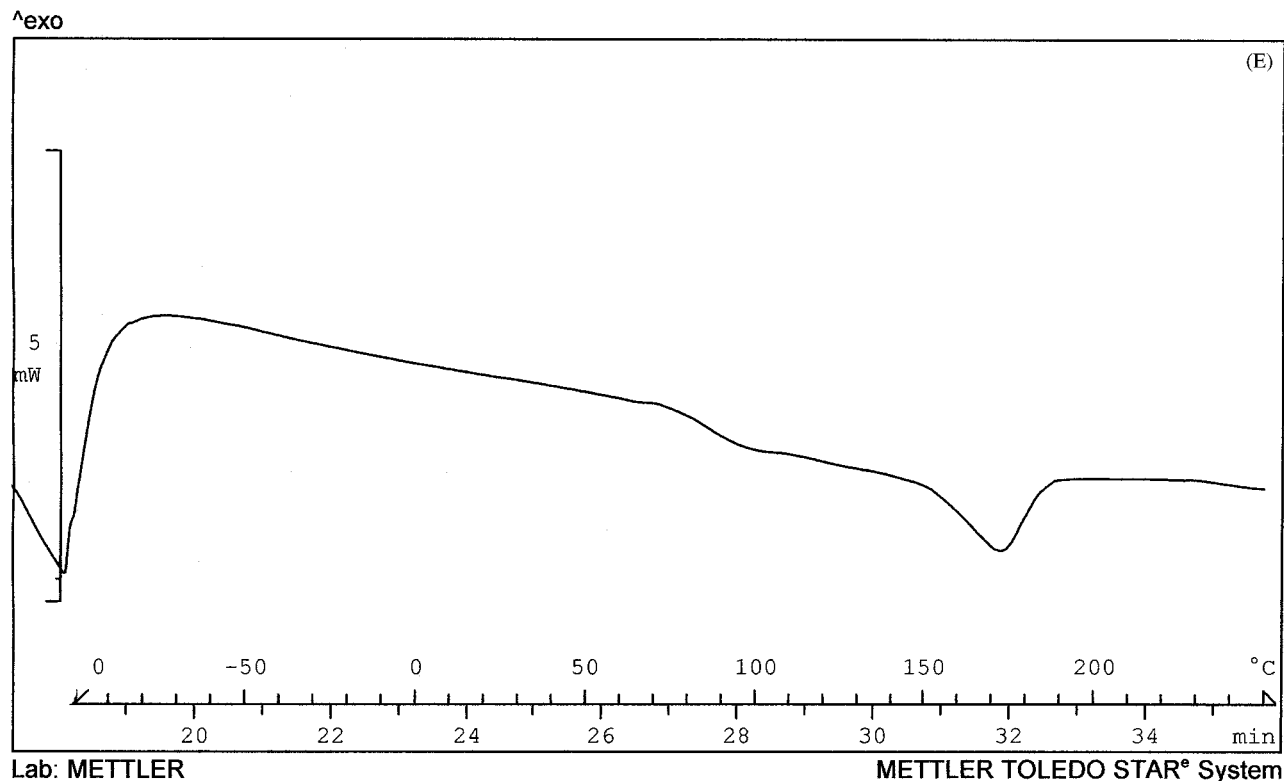


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zation of PVOH is obviously disturbed by the formation of a crosslinked structure. This is also the reason for an increase in the  $T_g$  of PVOH (from 70°C in neat PVOH to 86°C in PCL 50).

### Solarizing tests

The aim of this experiment is to verify thermal efficiency of the materials. Due to experimental difficulties in preparing regular films necessary for significant tests, we have limited the analysis to an area of  $120 \times 180$  cm for each PCL-x. Such films (around 50  $\mu\text{m}$  in thickness) have been deposited on the soil previously irrigated, and firmly hold on each side to avoid as much as possible lateral thermal losses. It is worth saying that the dimension of the test area is insufficient to make absolute evaluation of thermal data, but the test is relevant on a relative basis. Together with the three covered areas, a fourth area has been monitored without cover. Temperatures have been taken at a 0- and 10-cm depth with a digital thermometer, at intervals of 1 h from 9:00 a.m. to 12:00 p.m. every day, from 30th July to 14th August.

In Figure 3 the temperatures measured under the PCL 100 film, at a 0-cm depth, compared to the blank (uncovered soil), in a particular day are reported. It is evident how the film is able to cause an increase of the soil temperatures of about 20°C.

When this analysis is carried out at a 10-cm depth we still find temperatures of more than 5°C higher below the film, and such difference is maintained during the whole day.

Slightly reduced are the temperatures measured below the PVA-x-PCL 25 and 50, probably due to a reduced transparency of the films with increasing the crosslink density.

### Optical analysis

The prepared films have been subjected to optical analysis to verify their transparency in the UV-Vis

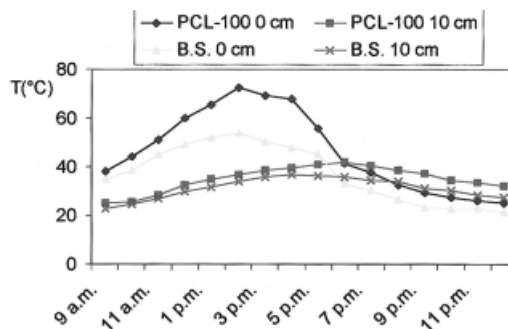


Figure 3 Soil temperatures measured at 0 and 10 cm depth under PCL 100 film and on bare soil (B.S.). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

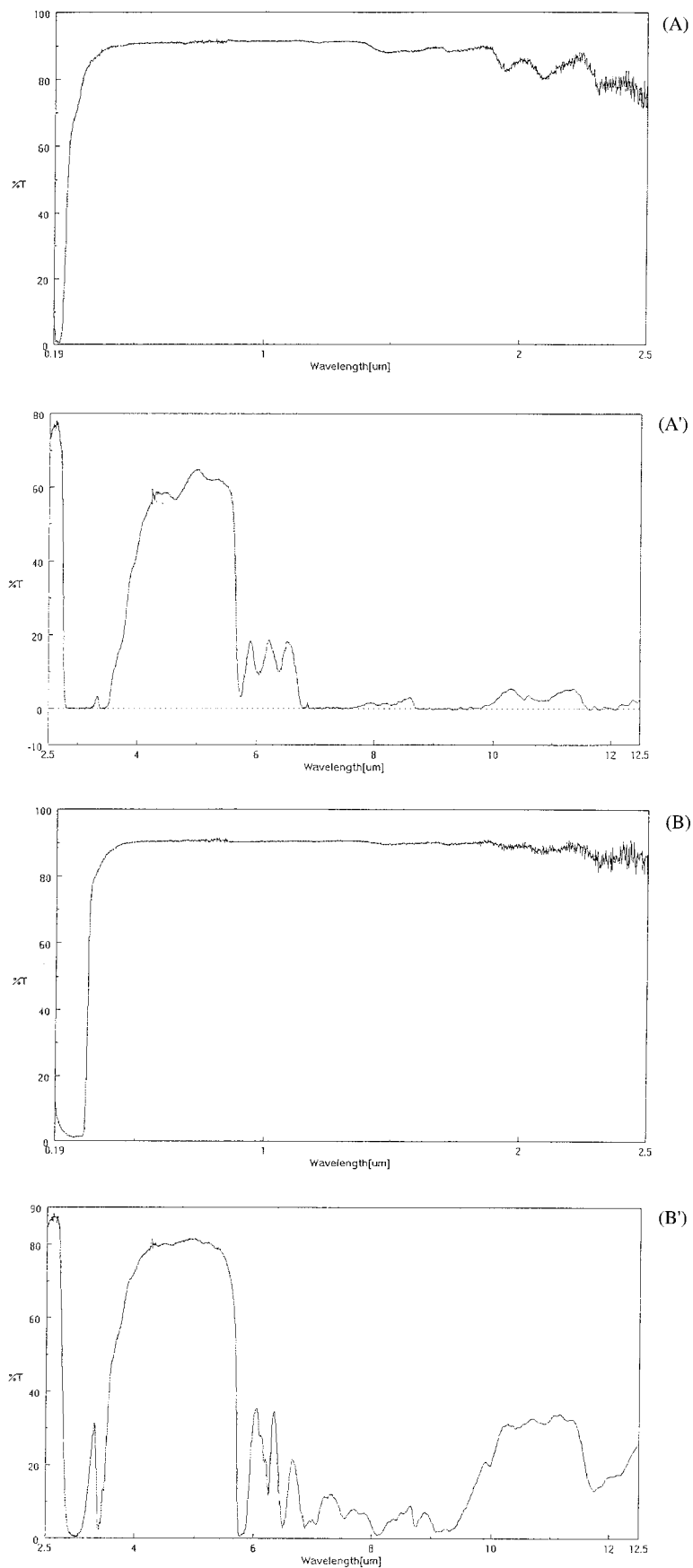


Figure 4 UV-Vis-IR total transmission spectra of: (A) PVOH; (B) PCL 25; (C) PCL 50; (D) PCL 100.



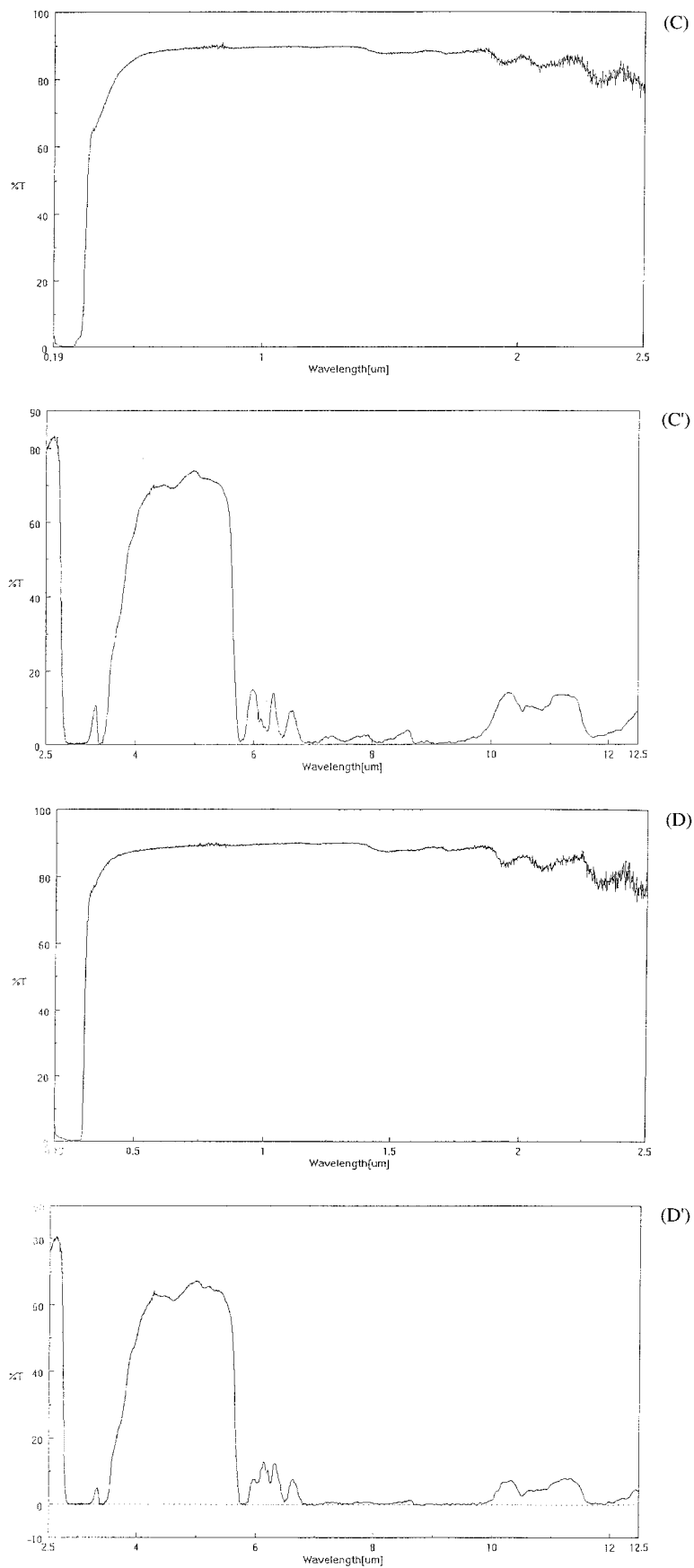
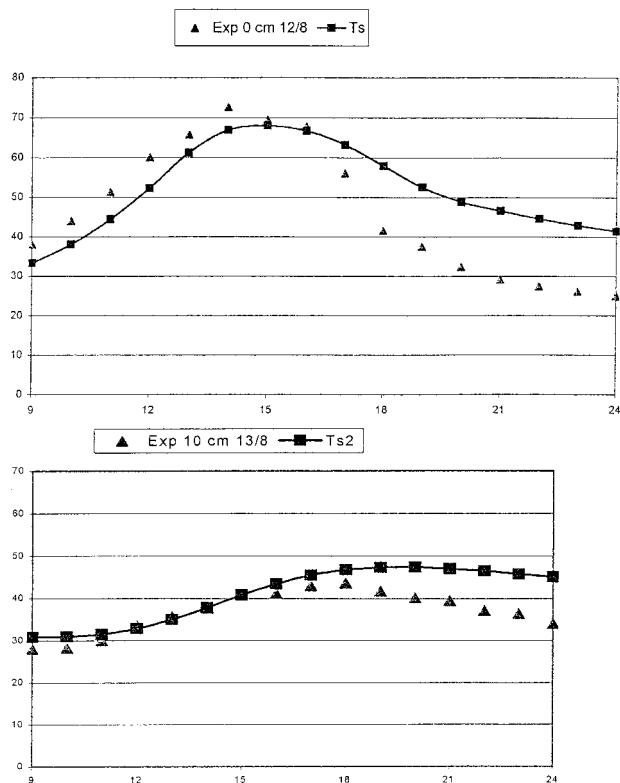


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**Figure 5** Thermal simulation of temperatures at 0 and 10 cm depth of soil covered with PCL 100 film (date: 13 Aug. 1998).

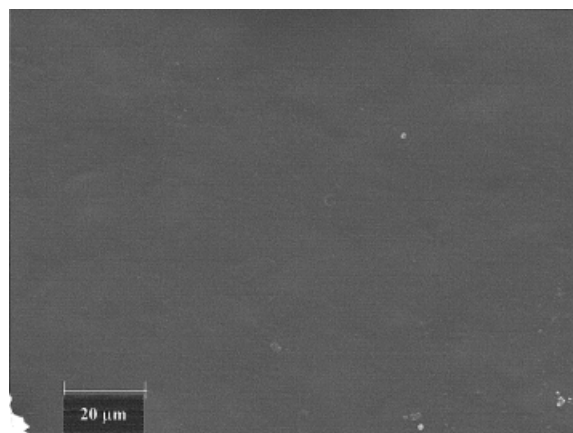
region, and their opacity to the IR radiation. The optical bench employed is able to record *in continuo* the UV-Vis-IR spectrum of the material from 0.19 to 12.5  $\mu\text{m}$ . The results, reported in Figure 4(A)–(D), show how all the films are highly transparent ( $\sim 90\%$ ) in the UV-Vis (PAR sensitive region), while the absorbance of the IR radiation in the region of 7–12  $\mu\text{m}$  is practically complete. It is worth noting that the progressive addition of increasing the amount of PCL to PVOH causes an increase in the transmittance of the IR radiation [see Fig. 4(A')–(D')]. This is due to the reduced IR absorbance of PCL if compared to PVOH. It is interesting to evaluate the results of a mathematical model able to simulate the thermal efficiency of a film and to compare them with the experimental data collected during the solarizing tests. The model assumes as input data the values of transmission coefficients of films as obtained from their spectra collected in the range of 0.19–12.5  $\mu\text{m}$ , and the thermal data (global and diffused solar radiation, open air temperatures, wind speed) for the period 13–15 August found in the meteorological reports of the region where the solarizing tests have been carried out. Details of the model can be found in published articles.<sup>13</sup> Essentially, the model organizes the physical situation into many isothermal subsystems: (a) film cover, (b) air layer below film cover, (c) soil surface, (d) soil layer.

For each subsystem, then, the model considers thermal exchange through conduction, convection, and irradiation, under the hypothesis of a totally sealed cover.

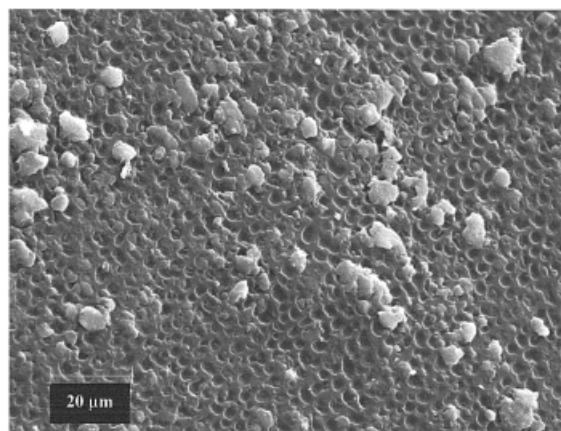
Thermal simulation, in terms of temperature vs. time, is reported in Figure 5 at 0 and 10 cm, and compared with the experimental data, on a particular day. The simulation of the thermal profile is rather satisfactory, particularly for the left side of the curve, which simulates soil heating. The right sides of the curves, which simulate thermal loss, predict a lesser decreasing of the soil and under soil temperatures. We believe that this can be ascribed to the irregular testing condition, due to the reduced dimension of the films, which renders influent contour conditions.

### Weathering of film

A qualitative analysis of the film, carried out by visual inspection, has revealed that, during exposition to environmental degradation, their behavior is a func-

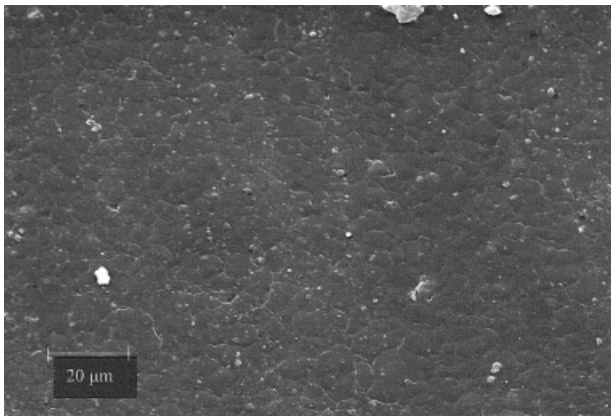


**Fig. 6A**



**Fig. 6B**

**Figure 6** Scanning electron micrographs of PCL 100 film surface after: (A) 0 and (B) 60 days of sun exposure.



**Figure 7** Scanning electron micrographs of PCL 25 after 60 days of sun exposure.

tion of the degree of crosslinking. As an overall observation, while neat PVOH film readily dissolves in rainy weather and is severely damaged in humid conditions, all the crosslinked films do not dissolve under rain. The only effect is that some diffuse opacity reverts when the films are dried.

At a microscopic level, environmental attack becomes evident. In Figure 6 is reported the appearance of PCL 100 film surfaces at the beginning and after 60 days of exposure. The level of damage of the film after 60 days, although still limited to the surface, is clearly evident as large cavities where the microbial attack can proceed. For comparison, in Figure 7 the appearance of PCL 25 film after a 60-day exposure is reported. It is evident that, at a high crosslink density, the kinetics of damage is slower and films tend to maintain their integrity for a longer time. It is then possible, by the present approach, to tailor the time of the functional life of the films, without imparting their final soil degradation.

### CONCLUSION

In the present article we have reported on the preparation and characterization of innovative PVOH-x-

PCL films whose composition is tailored to give different answers in terms of duration when applied as film coverage in protected cultivation. The degree of x-links, while maintaining the biodegradability of films, influences the thermal properties and the weather resistance. Of course, the films also show different mechanical properties as a function of the degree of x-links. This will be the content of a forthcoming article, where the mechanical properties will be also followed as function of exposition time.

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