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Blends of polyvinylalcohol and functionalised polycaprolactone. A study on the melt extrusion and post-cure of films suitable for protected cultivation

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A synthetic approach for the realisation of lifetime controlled biodegradable films is described starting from existing biodegradable polymers. Polyvinylalcohol (PVOH) chains are bridged through functionalised polycaprolactone (PCL) crosslinks directly during extrusion and film lamination. The resulting films are water resistant and their degradation may start only when buried in the soil due to microbial attack of the PCL bridges. The influence of blend composition on the mechanical properties and water sensitivity has been analysed. A thermal annealing is necessary after extrusion in order to complete the crosslinking of the obtained film. A mathematical model has been applied on the film to simulate their "greenhouse" effect. It was found that such films, when used as mulching film in agriculture, have a very interesting thermal response allowing temperatures inside the soil of 40–50°C, comparable to well known non biodegradable mulching films.

1. Introduction

Polymeric materials are widely used in agriculture, particularly for lightweight containers, irrigation pipes and coverage films (greenhouses, low tunnels, mulching and solarization, a technique that allows soil sterilization by means of direct sun light exposure) [1].

"Solarization" or "soil sterilisation by plastics" is an agricultural practice where a continuous film is applied on a pre-irrigated soil during the hottest season for the time necessary to kill (or at least de-vitalise) all pathogens by means of the increase in temperature (normally three to four weeks) [2]. 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 μm. Other pre-requirements of the film are a high barrier for gases (carbon dioxide, ethylene, and ammonia) produced by the soil microorganisms, and minimal thickness. Petrochemical derived plastics like polyethylene (PE) or poly (ethylene-co-vinylacetate) (EVA) are normally employed, posing serious problems of collection, disposal and reuse, particularly when used in direct soil contact, due to extreme lightness and dirtiness.

We have in recent years directed our research to develop biodegradable polymers to be proposed in agriculture in substitution of classical non-biodegradable plastics [3]. Many of these materials have originally been developed for the packaging industry. Starch-based blends, aliphatic polyesters, vinyl alcohol polymers are most successful examples. To apply them in agriculture, it is necessary to tailor their mechanical properties, optical and thermal behaviour and biodegradation time according to the different specific usage, i.e., in open field or under tunnels, in summer or winter climates, just to mention two most important variables. Among the above mentioned polymers, polyvinylalcohol (PVOH) has attracted our attention being a polymer that, upon plasticization, can be melt processed to form clear, tough films [4]. It is the only known C-C main

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chain polymer to be biodegradable through an enzymatic pathway that is highly accelerated by its water sensitivity. On the contrary, if PVOH is cross-linked with aldehydes, it becomes resistant to biodegradation.

In our approach, we are investigating the cross-linking of PVOH through the formation of biodegradable bridges made of functionalised polycaprolactone (PCL) [5]. In a previous study, we have prepared the films by solution means, while in the present paper, we report on an approach in the melt. Synthesis of functionalised PCL, melt preparation of reactive blends, thermal post-treatments of films, their spectroscopic and mechanical analysis are hereafter described. Moreover, we report also the UV-Vis-IR optical analysis of the obtained films and use it as input data for the simulation of their thermal behaviour in view of their application as "greenhouse film".

2. Materials and methods

2.1. Materials

Polyvinylalcohol (PVOH) is kindly supplied from Idroplast, Italy. It is a film grade formulation characterised by 96% hydrolysis of the original polyvinylacetate precursor of high molecular weight (>100.000 a.m.u.). It contains suitable plasticizers (glycerol based) which allows its melt processing at temperatures below 200°C. It is soluble in water already at moderate temperature (40–50°C). Polycaprolactone (PCL) is supplied pure from Solvay Interox. It has a $M_w = 2000$ a.m.u. and is hydroxyl terminated.

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

All solvents were purified according to standard procedures.

2.2. Preparation of a biodegradable film

PCL is reacted in solution with TDI (1 : 2 molar ratio) according to a procedure previously reported [5]. The reaction is monitored by FTIR spectroscopy. The final product, $PCL(NCO)_2$, is isolated and stored under nitrogen.

PVOH and $PCL(NCO)_2$ have been melt processed in a Brabender discontinuous mixer operating at different temperatures (180 and 200°C), different speeds of the cams (30 and 150 rpm) and different weight ratios of the constituent polymers: PVOH/$PCL(NCO)_2$ (100/25) and (100/50) ("RB" coded blends). For comparative purposes, also a PVOH/PCL (100/25) "mechanical blend" (MB) has been prepared in the same experimental conditions as the "reactive" blend. In a typical preparation, 100 g of PVOH (desiccated in vacuum at 100°C overnight) and 25 g of $PCL(NCO)_2$ (desiccated in vacuum at 60°C overnight) are fed into the mixing chamber at 180°C and mixing speed of 30 rpm. After 10 min the chamber is cooled under nitrogen while the blend is removed. Films are then obtained by compression molding the finely grounded material in a common heated press at temperature of 220°C for 10 min. The cross-linking reaction is followed by the disappearance, at FTIR, of the characteristic NCO vibration (2270 cm^{-1}). Occasionally, films are post cured by a vacuum treatment in an oven at 200°C.

2.3. Optical analysis

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 FT/IR 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 nm to 25000 nm for film thickness from 0.020 mm to 5.000 mm; measurements can be made also at variable angle from perpendicular to 60°.

2.4. Mechanical analysis

Mechanical analysis was carried out by using an Instron machine Mod. 1122 on compression moulded specimens of initial length 90 mm, initial width 10 mm and thickness 0.2 mm. The crosshead speed was fixed at 50 mm/min.

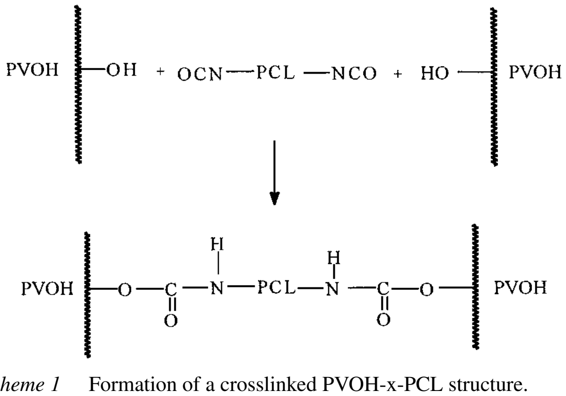
2.5. Solubility tests

Solubility tests were performed on water solutions (1% by weight) by using Hanna H193703 turbidimeter.

3. Results and discussion

In a search for biodegradable films suitable for application in solarizing coverage, we have identified polyvinylalcohol and polycaprolactone. 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 a very high barrier to gases and also a strong absorbancy in the thermal region. It is also biodegradable but has a very strong water sensitivity that impedes its use as solarizing film. PCL is, on the contrary, insoluble in water. It is reported to be compatible with PVOH [6].

In our study we have used PCL at low molecular weight to bridge chemically different PVOH chains (see Scheme 1).

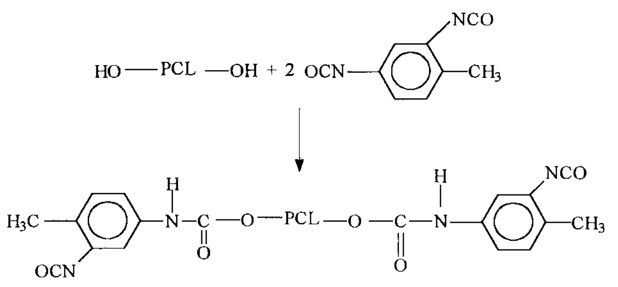


Scheme 1 Formation of a crosslinked PVOH-x-PCL structure.

By such method, we can reduce the water sensitivity of PVOH and render its film lifetime on the soil surface sufficient for the time necessary to effect the solarization. Once the film has been landfilled inside the same treated soil, anaerobic digestion of PCL bridges release free water soluble PVOH molecules which will undergo aerobic biodegradation.

3.1. Preparation of biodegradable reactive blends

To impart chemical reactivity to PCL towards PVOH, hydroxyl-terminated PCL has been reacted with diisocyanates (see Scheme 2).



Scheme 2 Formation of functionalised $PCL(NCO)_2$).

The reaction is carried out in a common solvent and 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 cm^{-1}. This polymer is still soluble and melts at about 60°C.

PVOH and $PCL(NCO)_2$ have been melt blended and the torque recorded during mixing [7]. The torque is a measure of the viscosity that, in turn, depends on the molecular weight and on the morphology of the molten system. In Fig. 1 we report torque as a function of mixing time of PVOH and mechanical and reactive blends (the behaviour of neat PCL cannot be recorded due to its very low melt viscosity).

The curves related to both blends are below that of PVOH, as a consequence of the addition of PCL. There are clear differences between MB and RB. In fact, while for MB and PVOH, as a consequence of progressive melting, torque diminishes in the first few minutes and then reaches a constant value, in the case of RB torque stays almost constant from the beginning. Moreover, the steady-state value of the RB system remains higher than that of the MB system. This is probably due to the advancement of the grafting reaction, which increases the viscosity, thus counterbalancing the effect of progressive melting. The advancement of the cross linking reaction (see Scheme 1) is checked also by the diminution of the characteristic $-N=C=O$ vibration at 2270 cm^{-1} and the simultaneous increase of the urethane stretching vibration at about 1550 cm^{-1}. It is to be stressed, anyway, that the sensitivity of the IR analysis is not very high, mainly due to the low molar amount of residual isocyanate groups. A more sensitive test has revealed to be the turbidity test reported in Table I. This test measures the optical transparency of solutions at a given concentration; in the present case, water has been used as solvent and a concentration of 1% by weight of the solute. The appearance of the solution of neat PVOH is very turbid, due to the presence of plasticizers, ester derivatives of glycerol, not water soluble. Also the mechanical blend is very turbid, as the system is not cross-linked and, together with PVOH plasticizers, the same PCL remains highly dispersed in water but not soluble. As a consequence, the values of turbidity for both solutions are higher than 1000 FTU. In the case of RB of same composition and thermal treatment, the value of turbidity decreases significantly. This can be ascribed to the incipient cross linking which renders the whole blend less water soluble thus avoiding also the release of plasticizers.

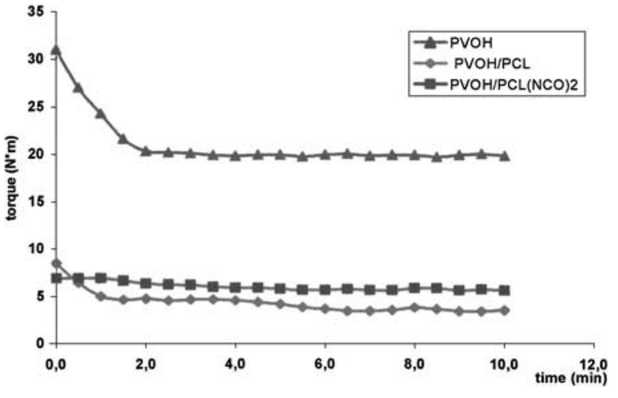


Figure 1 Torque as function of mixing time of neat PVOH, of PVOH/PCL (100/25) MB and of PVOH/PCL(NCO)2 (100/25) RB.

TABLE I Influence of processing conditions on turbidity values of PVOH and of MB and RB blends

Materials	T_{mix} (°C)	Mix. speed (rpm)	Mix. time (min)	Turbidity (FTU)
PVOH	180	30	10	>1000
PVOH/PCL (100/25) MB	180	30	10	>1000
$PVOH/PCL(NCO)_2$ (100/25) RB	180	30	10	890

TABLE II Influence of composition and processing conditions on the turbidity of $PVOH/PCL(NCO)_2$ RB blends

Composition	T_{mix} (°C)	Mix. speed (rpm)	Mix. time (min)	Turbidity (FTU)
$PVOH/PCL(NCO)_2$ 100/25	180	30	10	890
$PVOH/PCL(NCO)_2$ 100/25	180	150	10	121
$PVOH/PCL(NCO)_2$ 100/50	180	30	10	168

We have then investigated the possibility to advance as much as possible the reaction working on some processing parameters and verifying the effects on the final properties of blends. Assuming as reference a RB $PVOH/PCL(NCO)_2$ (100/25), processed for 10 min at 180°C at a rotating speed of the cams of 30 rpm, we have found of no use to increase the mixing time to 20 min or to increase the temperature to 200°C, as the only result is an increase of the degradation of the material. On the contrary it was revealed to be very useful to concentrate on the speed of rotation or to vary the blend composition. In Table II we can see that for the same 100/25 composition, increasing the speed of the cams to 150 rpm results in a strong reduction of turbidity. Similarly, when increasing the content of $PCL(NCO)_2$ in the blend (100/50) composition in Table II) a drastic reduction of the turbidity is recorded.

3.2. Post-cure of blend films

It is worth stressing that the event of complete cross-linking during melt mixing is unfavourable, from the point of view of workability of the blend. It can be assumed that, after a film extrusion step, a thermal treatment will be needed to complete the formation of a stable network. Hence, on the reactive blends, pressed into films, annealing experiments have then been conducted, with the aim to post-cure the materials. In fact, the thermal reaction between the hydroxyl groups of PVOH and the residual NCO end groups of PCL$(NCO)_2$ can be further advanced if carried out on thin films. On this basis, the RB PVOH/PCL$(NCO)_2$ (100/25) already processed at 180°C for 10 min at 30 rpm has been melt pressed in a common heated press at 200°C into films of different thicknesses that have been post-treated under vacuum at 200°C for different lengths of time, following the turbidity as cross linking parameter. The results are reported in Table III.

It is evident that both the parameters have a strong influence on the cross linking of the blends. In particular, cross linking is favoured by smaller thicknesses (reduced turbidity) and by annealing time longer than 10 min. We can assume that such conditions are the most favourable for the complete condensation of less reactive PCL isocyanates and pendant hydroxyl groups of PVOH. As a matter of fact, a similar treatment carried out on a mechanical blend film does not produce any change in the behaviour of the material. In order to produce a visual evidence of the influence of the thermal treatments on the physical state of samples, in Figs 2 and 3 are reported, respectively, the photos of the appearance of a water solution for a group of samples of different thickness annealed for the same time length, and that for a group of samples of same thickness annealed at different time length.

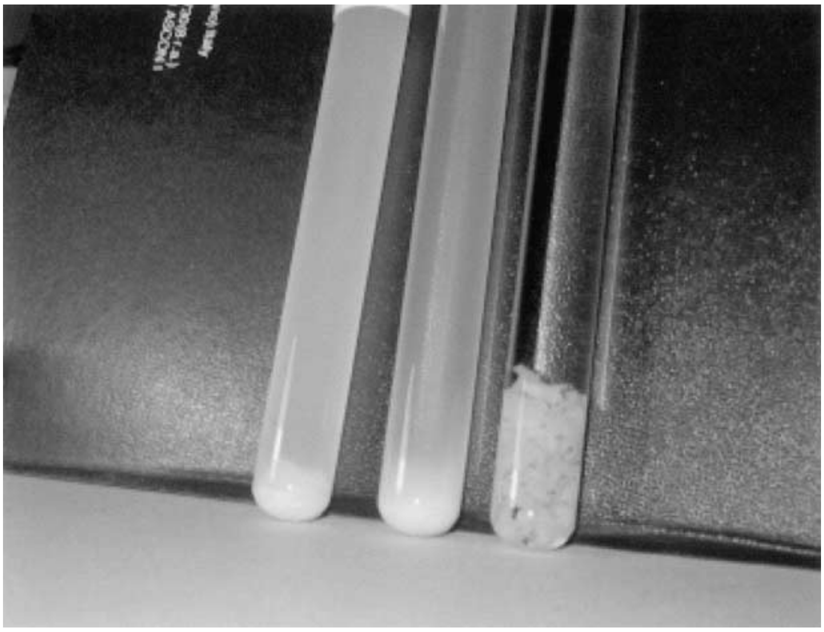


Figure 2 Appearance of water solutions of a PVOH/PCL$(NCO)_2$ (100/25) RB processed at 30 rpm and annealed at 200°C for the same time length (20 min). Influence of sample thickness on turbidity. From left: 1 mm, 0.5 mm, 0.15 mm.

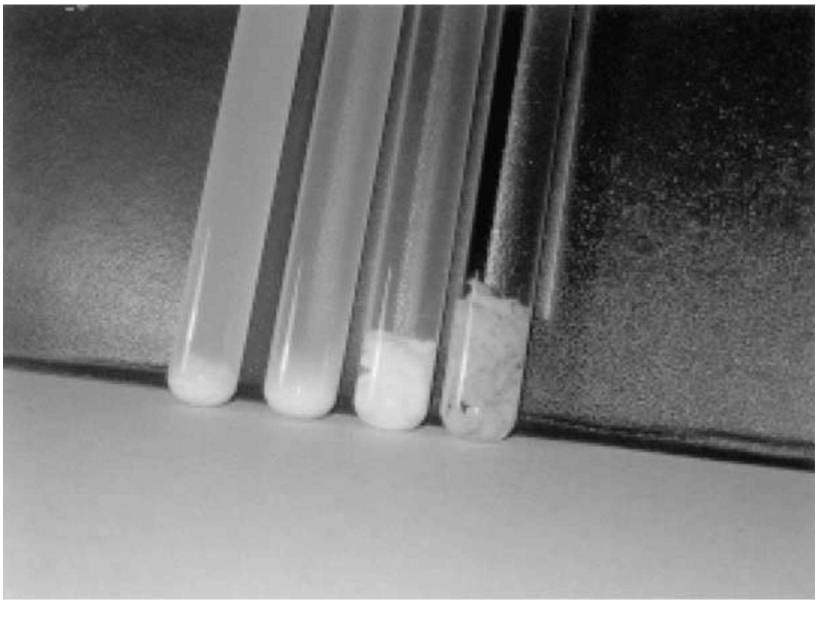


Figure 3 Appearance of water solutions of a 0.15 mm film made of a PVOH/PCL$(NCO)_2$ (100/25) RB, processed at 30 rpm and annealed at different time lenghts. Influence of the annealing time on the turbidity. From left: 3 min, 6 min, 10 min, 20 min.

TABLE III Turbidity values as function of thickness and of annealing time for the PVOH/PCL(NCO)$_2$ (100/25) RB

	Annealing time (min)					
Thickness (mm)	0	3	6	10	20	30
1	890	720	584	43	3.6	1.38
0.5	890	545	503	33	2.56	0.28
0.15	890	430	176	2.48	0.07	0

TABLE IV Main mechanical parameters of PVOH and PVOH/PCL blends

Materials	Modulus (MPa)	TS (MPa)	EB (%)
PVOH	150	24	200
PVOH/PCL (100/25)	130	20	250
PVOH/PCL(NCO)$_2$ (100/25)	105	17	200

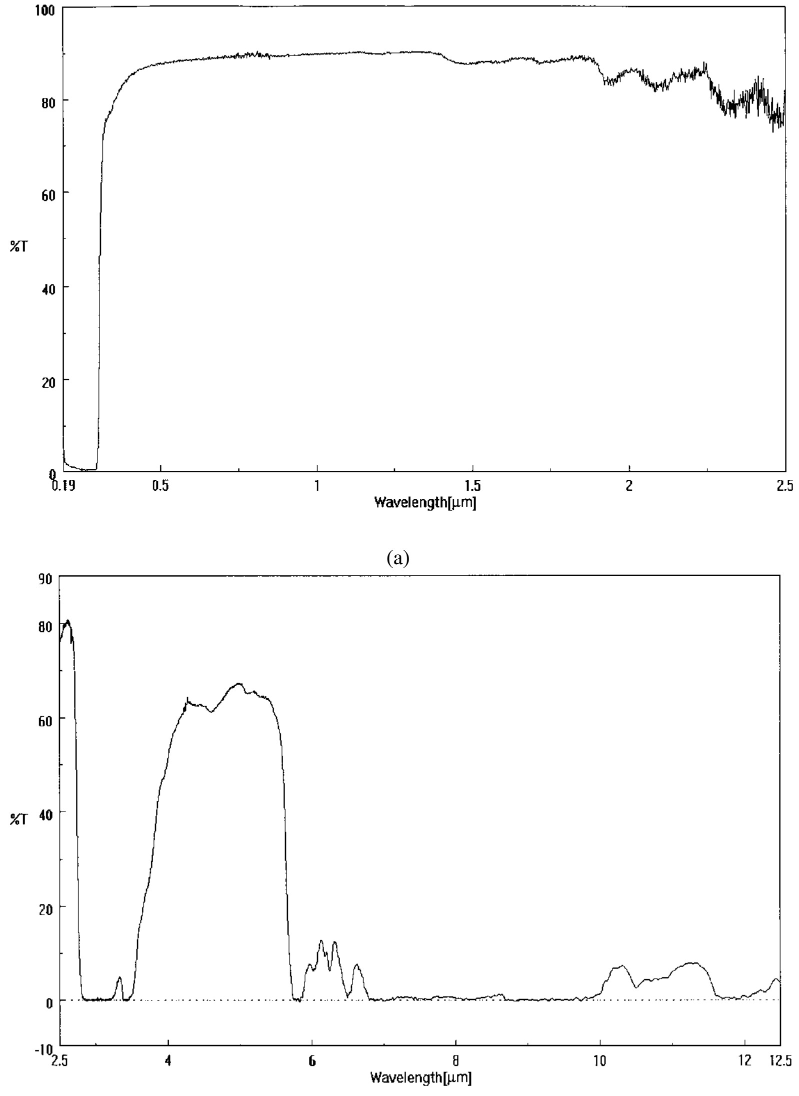
3.3. Mechanical analysis

Mechanical testing of PVOH and its blends has allowed the evaluation of the influence of PCL, either modified or hydroxyl terminated, on the behaviour of PVOH. In both type of blends a slight worsening of mechanical properties is observed, as evidenced by the diminution of modulus and of tensile strength (TS). On the contrary, the elongation at break (EB) seems not to be negatively influenced by the addition of PCLs. Moreover, not functionalised PCL seems to act as a plasticiser towards PVOH, as evidenced by the increase of EB (see Table IV). We have then evaluated the influence of the processing conditions on the mechanical performances of PVOH/PCL(NCO)$_2$ RB.

The blend processed at 150 rpm shows higher modulus and lower elongation at break if compared with the same blend worked at reference conditions. This finding is indicative of an enhanced rigidity probably due to the formation of cross-links. The degradation caused by the increase of temperature is clearly demonstrated by the worsening of all the mechanical properties. The 10 min annealing carried out on the PVOH/PCL(NCO)$_2$ (100/25) blend processed in standard conditions has caused a strong increase of rigidity, as shown by the three fold increase of the modulus (see last row of Table V).

3.4. Optical analysis

In view of their application as thermal films in agriculture, the cross-linked PVOH/PCL films must be characterized by a good "greenhouse" efficiency, i.e., they must be transparent to incident solar radiation and be



(a)

(b)

Figure 4 UV-VIS-NIR (a) and IR (b) of PVOH/PCL(NCO)$_2$.

TABLE V Main mechanical parameters of PVOH/PCL$(NCO)_2$ RB as function of processing conditions

PVOH/PCL$(NCO)_2$ composition	Processing conditions	Modulus (MPa)	TS (MPa)	EB (%)
(100/25)	180°C 30 rpm	105	17	200
(100/25)	180°C 150 rpm	160	12	165
(100/25)	200°C 30 rpm	60	11	50
(100/50)	180°C 30 rpm	137	14	145
(100/25)	180°C 30 rpm + 10 min annealing	305	21	93

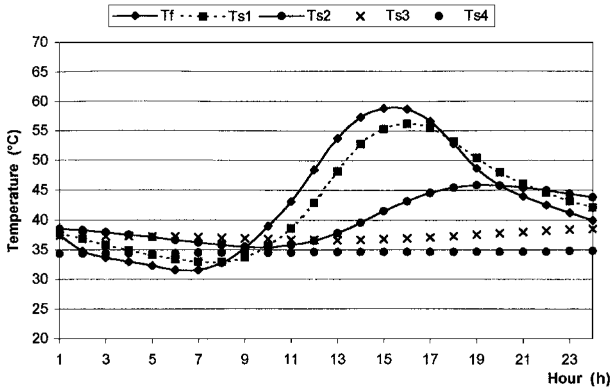


Figure 5 Numerical results of the simulation performed on a typical PVOH/PCL$(NCO)_2$ film. It has been represented the soil temperature at different depths. Tf: soil temperature at 1 cm; Ts1: soil temperature at 5 cm; Ts2: soil temperature at 15 cm; Ts3: soil temperature at 30 cm; Ts4: soil temperature at 50 cm.

opaque to the thermal losses from the soil. The films prepared have then been subjected to optical analysis to verify their transparency in the UV-Vis 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. The result reported in Fig. 4 shows how a typical PVOH/PCL$(NCO)_2$ film is highly transparent (>90%) in the UV-Vis, while the absorbance of the IR radiation in the region 7–12 μm is practically complete. The above spectra have been used, together with some other input data (*external air temperature, external air humidity, wind velocity, soil emittance, sky emittance, etc.*) to build up a mathematical model of simulation, which allows prediction of the thermal heating of a soil covered by the film [3]. The result of the simulation, reported in Fig. 5, shows that the temperatures reached below the film are rather high and still at 100 mm depth a temperature of 47°C is recorded. Such a temperature profile is not dissimilar from the typical profile of a thermal ethylene-co-vinylacetate (EVA) film, thus proving that this PVOH-based polymer is a promising candidate for the realisation of biodegradable thermal films in agriculture [8].

4. Conclusion

The introduction of chemical bridges of polycaprolactone onto the base structure of polyvinylalcohol directly during the extrusion process allows the realization of biodegradable films whose main characteristics are the improvement of water resistance and the tailoring of mechanical properties. The cross-linking process is completed by means of post-extrusion annealing of the films. The obtained materials have been characterized in their optical behaviour, and their UV-Vis-IR spectrum is consistent with its application as thermal film in agriculture, as confirmed by a mathematical simulation.

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