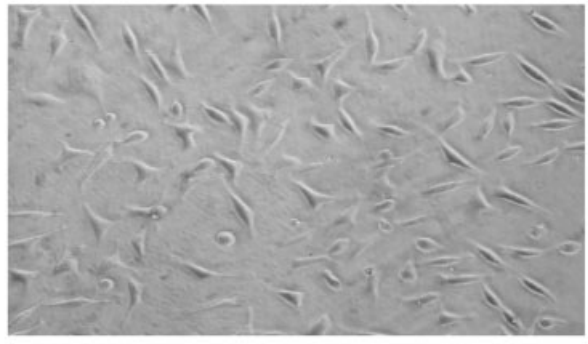
Summary: Syntheses of wholly natural polymeric linseed oil (PLO) containing peroxide groups have been reported. Peroxidation, epoxidation and/or perepoxidation reactions of linseed oil, either under air or under oxygen flow at room temperature, resulted in polymeric peroxides, PLO-air and PLO-ofl, containing 1.3 and 3.5 wt.-% of peroxide, with molecular weights of 2 100 and 3 780 Da, respectively. PLO-air contained cross-linked film up to 46.1 wt.-% after a reaction time of 60 d, associated with a waxy, soluble part (PLO-air-s) that was isolated with chloroform extraction. PLO-ofl was obtained as a waxy, viscous liquid without any cross-linked part at the end of 24 d under visible irradiation and oxygen flow. Polymeric peroxides, PLO-air-s and PLO-ofl initiated the free radical polymerization of both methyl methacrylate (MMA) and styrene (S) to give PMMA-*graft*-PLO and PS-*graft*-PLO graft copolymers in high yields with $\overline{M}_w$ varying from 37 to 470 kDa. The polymers obtained were characterized by FT-IR, ^{1}H NMR, TGA, DSC and GPC techniques. Cross-linked polymers were also studied by means of swelling measurements. PMMA-*graft*-PLO graft copolymer film samples were also used in cell-culture studies. Fibroblast cells were well adhered and proliferated on the copolymer film surfaces, which is important in tissue engineering.



Proliferation of the fibroplast cells on the PS-*graft*-PLO film.

Synthesis and Characterization of Polymeric Linseed Oil Grafted Methyl Methacrylate or Styrene

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Introduction

More attention is being paid to studying and developing environment biodegradable plastics in order to retard or eradicate plastic pollution.[1,2] Current interest in cheap biodegradable polymeric materials has recently encouraged the development of such materials from readily available, renewable, inexpensive natural sources such as starch, polysaccharides and edible oils.[3] Today, natural oils and fats are considered to be the most important class of renewable sources for the production of biodegradable polymers. Biodegradable microbial polyesters, poly-(3-hydroxy alkanoates), can be produced by certain bacteria from carboxylic acids obtained from plant oils and fish oils[4] as well as a wide variety of carbon substrates such as fructose and glucose.[5] Furthermore, considerable research efforts have been focused on the direct synthesis of copolymers of oils with synthetic polymers. With regard to this fact, copolymerization of oils with styrene,[6] divinylbenzene-styrene[7] and the cationic polymerization of epoxidized drying oils[8] have been reported. Linseed oil is the most widely used drying oil in paint formulation and for varnishes and raw materials for uralkyds and alkyd resins.[9,10] Aliphatic polyanhydrides derived from fatty acids have been used as carriers for controlled drug delivery.[11] On the other hand, cell adhesion and proliferation on biodegradable polymer films are important in tissue engineering.[12]

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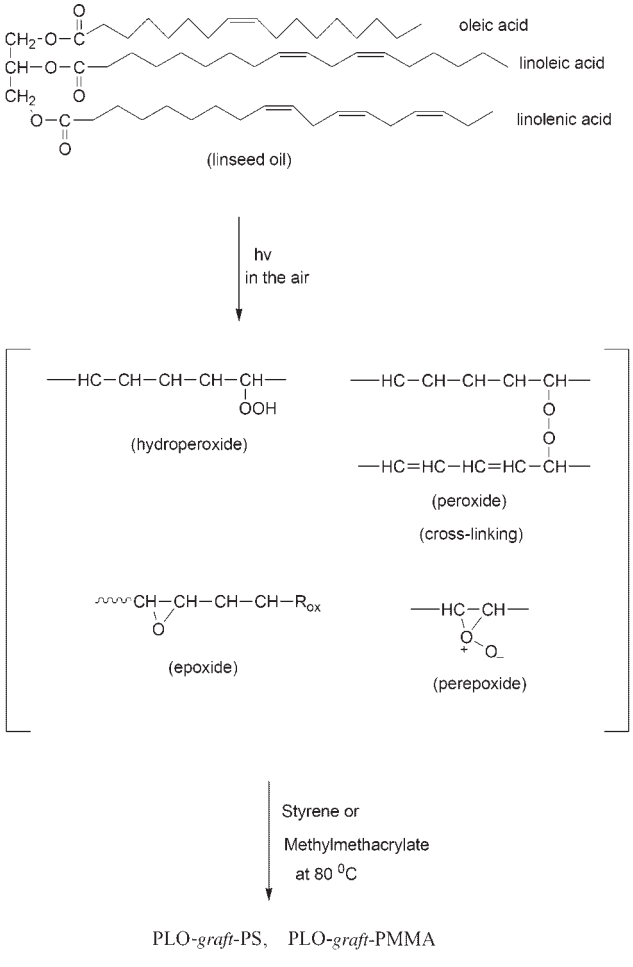
Naturally occurring linseed oils are triglycerides consisting of a mixture of saturated and unsaturated (oleic, linoleic and linolenic) fatty acids which can be modified via hydroperoxide, peroxide, epoxide and perepoxide formation.[10,13] The oxidation of linseed oil in the air involves hydrogen abstraction on a methylene group between two double bonds in the polyunsaturated fatty acid chain. This leads to conjugated hydroperoxides in a majority and radical recombination produces cross-linking.[9] Perepoxides and epoxides can also be obtained by the oxidation of the oil.[13] The oxidation of linseed oil via epoxide, peroxide and perepoxide intermediates can be designed as indicated in Scheme 1.

This work refers initially to the polymerization of linseed oil via peroxide linkages during the drying process in the air or under oxygen flow and then to the use of this polymeric peroxide in the polymerization of vinyl monomers to obtain graft copolymers containing oily segments leading to biodegradability and biocompatibility.



Scheme 1.

Experimental Part

Materials

Linseed oil was supplied by Aldrich and used as received. Styrene and methyl methacrylate monomers supplied were from Aldrich and were freed of inhibitor by vacuum distillation over CaH_2. All other chemicals were reagent grade and used as received.

Formation of Polymeric Linseed Oil under Laboratory Conditions

For the formation of polymeric linseed oil, 20 g of linseed oil was spread out into a petri dish ($\phi = 16$ cm) and introduced to sunlight in the air at room temperature. After a given time, a gel polymer film associated with a waxy and viscous liquid occurred. With chloroform extraction of the crude polymeric oil for 24 h at room temperature, the soluble part of the polymeric linseed oil (PLO-air-s) was separated from the gel (PLO-air-g). The peroxygen analysis of the PLO-air-s gave 1.3 wt.-%, $\bar{M}_w = 2\,100$ Da and MWD = 1.92. The results and conditions of the polymer formation of linseed oil are listed in Table 1.

Formation of Polymeric Linseed Oil under O_2 Flow

For the preparation of polymeric linseed oil (PLO-ofl) under O_2 gas, 10 g of linseed oil was placed into a 250 mL round bottom flask. O_2 gas was introduced to the linseed oil at a rate of 3–4 bubbles per minute with light from a 100 W bulb at room temperature for 24 d. The peroxygen analysis of the wholly soluble viscous liquid gave 3.5 wt.-%, $\bar{M}_w = 3\,780$ Da and MWD = 1.81.

Peroxygen Analysis

Peroxygen analysis of the soluble PLO fractions was carried out by refluxing a mixture of isopropanol (50 mL)/acetic acid (10 mL)/saturated aqueous solution of KI (1 mL) and 0.1 g of the polymeric sample for 10 min according to the literature.[14]

Graft Copolymerization

For graft copolymerization of PLO-peroxides with a vinyl monomer, a given amount of PLO, styrene or methyl methacrylate was charged separately in a pyrex tube. Argon was introduced through a needle into the tube for about 3 min to expel the air. The tightly capped tube was then put into a water bath at 80 °C. After the required time, the contents of the tube were coagulated in methanol. The graft copolymer samples were dried overnight under a vacuum at 30 °C. The characteristic data of styrene and methyl methacrylate polymerization initiated by the PLO-peroxides are listed in Table 2.

Fractional Precipitation of the Graft Copolymers

Graft copolymer samples free of their related homopolymers (homo PS or homo PMMA) and unreacted PLO were obtained by adding a non-solvent (MeOH) to their solution ($CHCl_3$) via a fractional precipitation method reported in ref.[15] γ-Values

Table 1. Reactions and conditions of polymeric film formation of linseed oil in the air at room temperature.

Run no	Linseed oil	Time	Polymer yield			q_w [a]
	g	d	Total	Soluble	Cross-linked	
			g	wt.-%	wt.-%	
50-1	5.12	3	3.39	80.3	19.7	10.2
50-2	5.14	7	5.05	67.8	32.2	12.9
50-3	5.09	15	5.09	72.7	27.3	9.9
50-4	5.11	30	5.10	61.0	39.0	11.0
50-5	5.07	60	5.07	53.9	46.1	7.8

[a] Swelling ratio of the crosslinked PLO.

were calculated as the ratio of the total volume of MeOH to $CHCl_3$ solution of the graft copolymer as the polymer began to precipitate. The fractionated polymer was dried under a vacuum.

Polymer Characterization

FT-IR spectra were obtained using a Jasco FTIR-300 E spectrometer. ^{1}H NMR spectra were recorded in $CDCl_3$ at 17 °C with a tetramethylsilane internal standard using a 400 MHz NMR AC 400 L. The molecular weight of the polymeric samples was determined by gel permeation chromatography (GPC) with a Waters model 6000A solvent delivery system having a model 401 refractive index detector and a Mode 730 data module and with two Ultrastyragel linear columns in series. Chloroform was used as the eluent at a flow rate of 1.0 mL · min^{-1}. A calibration curve was generated with polystyrene standards.

Differential scanning calorimetry (DSC) thermograms were taken on a Netzsch DSC 204 with CC 200 liquid nitrogen cooling system in order to determine the glass transition temperatures (T_g). Thermogravimetric analysis (TGA) of the polymers obtained was performed on a PL TGA 1500 instrument to determine thermal degradation. For DSC analysis, samples were heated from −50 to +150 °C in a nitrogen atmosphere at a rate of 10 °C · min^{-1}.

Swelling Measurements

The swelling degrees of cross-linked graft copolymers obtained at equilibrium were determined by gravimetry at room temperature in $CHCl_3$. Swelling ratios, q_v, were calculated using the volume ratio of swollen polymer ($v_{\text{swollen polymer}}$) to dry polymer ($v_{\text{dry polymer}}$).[16]

Cell Culture and Cell Adhesion Studies

The murine fibroblast cell line L-929 was obtained from American Type Culture Collection (ATCC, Rockville, MD, USA). L-929 cells were cultivated in coated polymer films and uncoated standard polystyrene dishes (60 mm diameter). Cultures on the polymer films sterilized by ethylene oxide were maintained at 37 °C under air with 5 wt.-% of CO_2, with 99% relative humidity. The cells were routinely grown in an RPMI-1640 medium containing 10 wt.-% of fetal bovine serum (supplied from Gibco, USA) without antibiotics. Cells were

Table 2. Reactions and conditions for the polymerization of vinyl monomers initiated by soluble PLO at 80 °C for 7 h.

Run No	PLO-air-s	PLO-ofl	St	MMA	Polymer Yield			Molecular weight	
	g	g	mL	mL	Total	Crosslinked[a]	q_v[b]	$\bar{M}_w \times 10^4$	MWD
					g	wt.-%			
39-5	0.50	–	5	–	3.80	78.6	53.7	12	2.82
51-2	0.50	–	5	–	4.26	73.9	54.7	–	–
51-1	0.50	–	3	–	2.14	42.6	24.3	–	–
39-6	0.50	–	–	5.0	2.23	4.6	–	47	1.97
51-3	0.50	–	–	3.0	1.80	21.2	–	–	–
48-1	0.42	–	–	2.5	1.14	23.8	21.2	33	1.14
41-2	0.51	–	–	1.0	0.37	54.7	14.3	–	–
55-3	–	1.00	–	1.1	0.87	–	–	3.7	1.32
55-4	–	1.00	–	2.2	1.11	–	–	7.8	1.41
55-2	–	1.01	–	3.2	2.54	–	–	6.0	1.55

[a] The rest of the percentage is soluble polymer.
[b] Swelling ratio of the cross-linked polymer.

visualized in an inverted microscope with 400× magnification using phase-contrast mode (Nikon Eclipse TE 300, Tokyo, Japan). A Minolta Dimage 7i camera was used to take photographs of the growing cells.

Results and Discussion

Polymeric Linseed Oil Containing Peroxide Groups

Two types of polymeric linseed oil (PLO) containing peroxide groups were obtained by peroxidation, epoxidation and/or perepoxidation reactions of linseed oil either under air (PLO-air) or under oxygen flow (PLO-ofl) at room temperature.

The film formation of linseed oil in the air under laboratory conditions was followed with time as tabulated in Table 1. PLO-air samples contained cross-linked films associated with a waxy, soluble part (PLO-air-s) that was isolated with the chloroform extraction. Cross-linked polymer formation in the crude polymeric linseed oil increased with time from 19.7 wt.-% to 46.1 wt.-%. The swelling degree of the cross-linked PLOs in $CHCl_3$ changed from 7.8 to 12.9. We can say that cross-linking density increases with time as well as the increase in the cross-linked part. The peroxygen content of the PLO-air-s samples was nearly the same as the 1.3 wt.-% and $\overline{M}_w$ of the PLO obtained from linseed oil polymerized for 60 d (run no. 50-5 in Table 1), which was 2 100 Da, with a MWD of 1.92. The peroxygen content of PLO-ofl samples was found to be 3.5 wt.-%. The $\overline{M}_w$ of the PLO-ofl was 3 780 Da, with a MWD of 1.81.

PLO-ofl was obtained as a waxy, viscous liquid without any cross-linked part after 24 d under visible irradiation and oxygen flow. The gel polymer film on the waxy viscous liquid started to form after the 26th day. The PLO-ofl initiator used in the vinyl polymerization was taken from the reaction vessel at the end of the 24th day, before starting the cross-linking.

Graft Copolymerization

PLO-peroxides initiated the polymerization of MMA or S at 80 °C to obtain PMMA-*graft*-PLO and PS-*graft*-PLO in high yields. The copolymerization conditions and copolymer analysis are listed in Table 2. Cross-linked and soluble graft copolymer fractions were isolated by means of chloroform extraction. The cross-linked part of the PS-PLO graft copolymer was higher than that of the PMMA-*graft*-PLO graft copolymer. Swelling measurements of the cross-linked graft copolymers were also measured to calculate q_w values. The cross-link density increased with a rise in the PLO concentration in feeding.

Soluble fractions of the graft copolymers were fractionally precipitated to isolate graft copolymers from their related homopolymers. Homo PS and homo PMMA were precipitated in the γ range 0.7–1.0 and 3.0–3.6 respectively, while PLO-*graft*-PS and PLO-*graft*-PMMA copolymer fractions were precipitated in the range 0.4–2.0 and 2.0–4.0, respectively. Because PLO was completely soluble in the mixture of chloroform and methanol, homo PLO was exactly isolated from the crude graft copolymer. Since the γ values of the graft copolymers cover those of the homo PMMA, we cannot say that graft copolymer was isolated from homo PMMA. Linseed oil polymer inclusion shifts the γ value of the graft copolymers to somewhat higher ranges.

Figure 1 shows the FT-IR spectrum of a PLO-*graft*-PS sample (39-5). The FT-IR spectrum of sample 39-5 shows the characteristic absorption peaks of a phenyl group at 699 cm^{-1}, 1 600 cm^{-1} and signals of the double bonds in

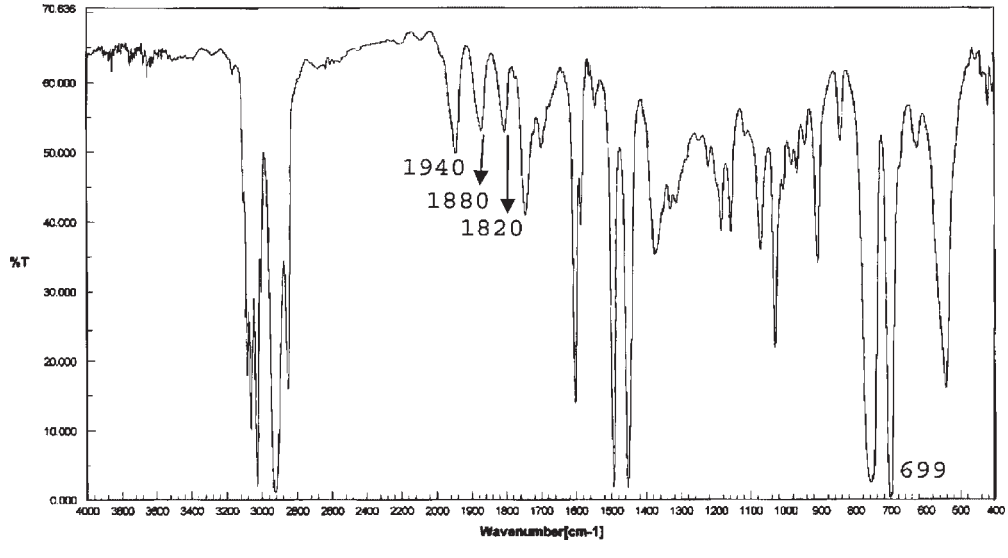


Figure 1. FT-IR spectrum of the PLO-*graft*-PS block copolymer sample (39-5).

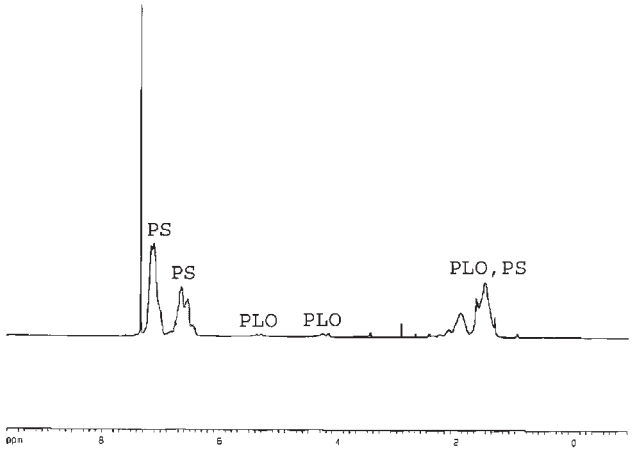


Figure 2. ^{1}H NMR spectrum of the PLO-*graft*-PS block copolymer samples (39-5).

PLO at 2 900 cm^{-1}. Carbonyl stretching appears between 1 735 and 1 750 cm^{-1}.

The ^{1}H NMR spectrum of the soluble part of PLO-*graft*-PS (39-5) shows characteristic peaks as indicated in Figure 2.

^{1}H NMR: $\delta = 0.85$ (–CH_3), 2.8, 2.2, 1.5 (–CH_2–), 6.4–6.6, 7.0–7.2 (phenyl group of styrene).

The peaks at 4.1–4.4 ppm originate from the protons in the methylene groups of the triglyceride. The vinylic protons are detected at 5.3 ppm. For this sample, PLO inclusion was found to be 19 mol-% by taking the ratio of the signals at 7.0 and at 4.1 ppm.

^{1}H NMR spectra of the soluble copolymer samples of PLO-*graft*-PMMA (BC: 39-6, γ: 2.0–4.0) contained characteristic peaks as indicated in Figure 3 and 4. The –COOC$\underline{H_3}$ of MMA appears at 3.7 ppm and the –C$\underline{H_2}$– of LO appears at 2.8, 2.3, 1.9, 1.9, 1.3 and 0.9 ppm. The peaks at 4.1–4.4 ppm originate from the protons in the methylene groups of the triglyceride. The vinylic protons were detected at 5.3 ppm. From Figure 3, the PLO inclusion was found to be 12 mol-% by taking the ratio of the signals at 3.7 and 4.1 ppm and from Figure 4 the PLO inclusion was found to be 24 mol-% by taking the ratio of the signals at 3.7 and 4.1 ppm.

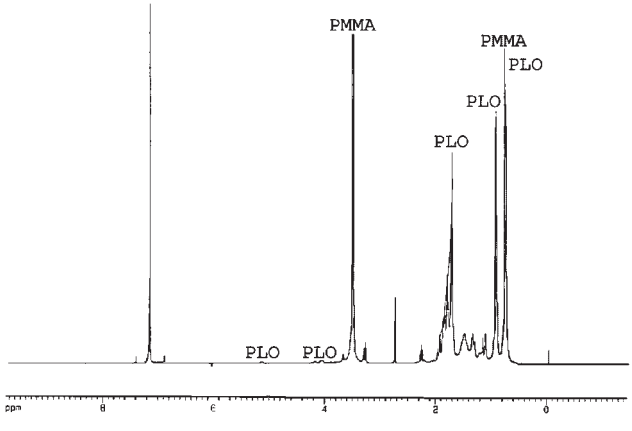


Figure 3. ^{1}H NMR spectrum of PLO-*graft*-PMMA block copolymer sample (39-6).

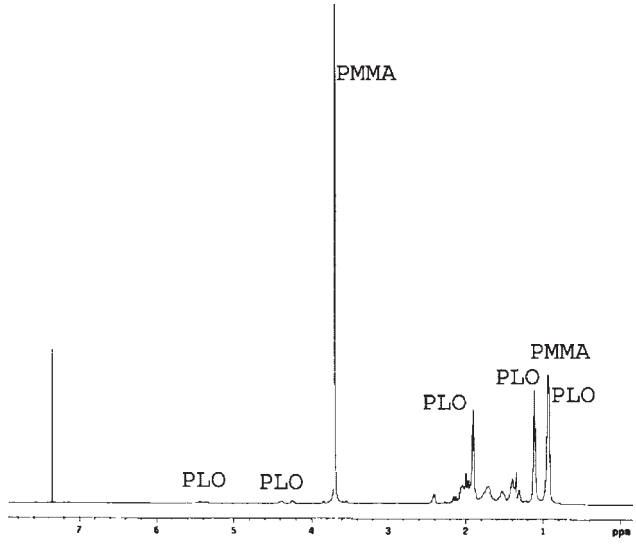


Figure 4. ^{1}H NMR spectrum of PLO-*graft*-PMMA block copolymer sample (55-2).

GPC was used to determine the molecular weights and the polydispersity of PLO and the graft copolymers. Fractionated samples of PS-*graft*-PLO and PMMA-*graft*-PLO gave unimodal GPC chromatograms. Figure 5 includes the unimodal GPC traces of the graft copolymer samples, which can be attributed to the pure graft copolymer without homo PMMA adduct.

Thermal analysis of the graft copolymers was performed by DSC and TGA. Figure 6 indicates the thermogravimetric traces of soluble and cross-linked PS-*graft*-PLO graft copolymers and soluble and cross-linked PLOs. The first temperature region at around 150 °C is mainly due to evaporation

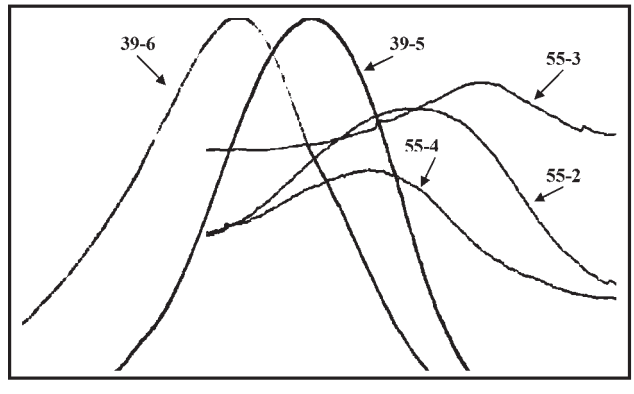


Figure 5. GPC chromatograms of PS-*graft*-PLO (39-5) and PLO-*graft*-PMMA (39-6, 55-2, 55-3, 55-4) graft copolymer samples.

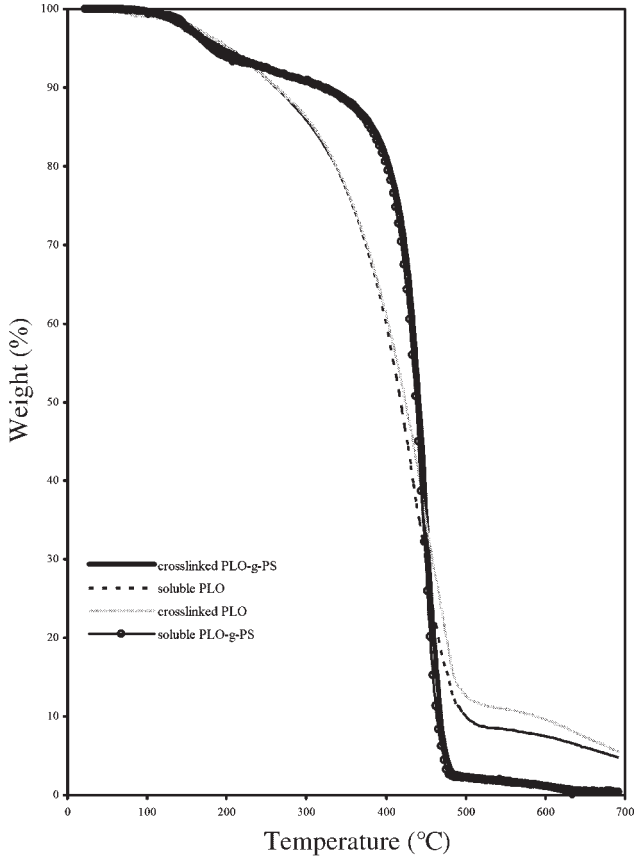


Figure 6. Thermogravimetric traces of PS-*graft*-PLO graft copolymer (39-5), cross-linked PLO (50-5) and soluble PLO (50-5).

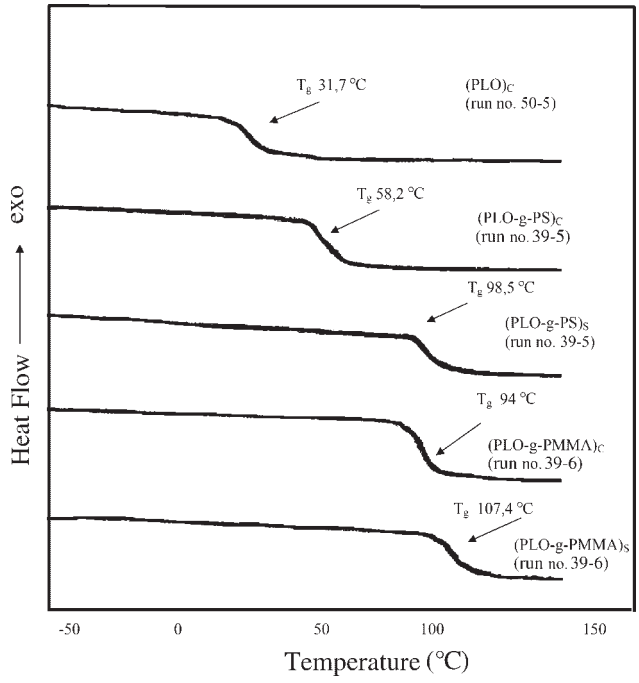


Figure 7. DSC traces of cross-linked (c) and soluble (s) PLO homo and copolymers: cPLO (run no. 50-5), cPLO-*graft*-PS (run no. 39-5), sPLO-gPS (run no. 39-5), cPLO-*graft*-PMMA (run no. 39-6), sPLO-*graft*-PMMA (run no. 39-6).

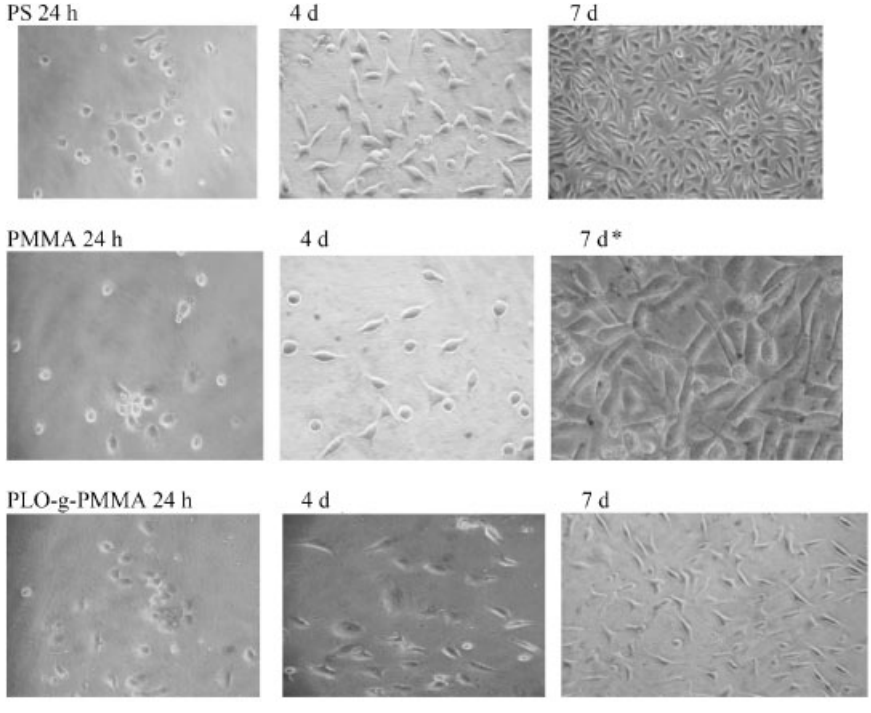


Figure 8. Cell photographs on the polymer films. Magnification: 400× (*Magnification: 1 000×).

and decomposition of the unreacted free oil in the bulk polymer. The second stage corresponds to degradation and char formation of the cross-linked polymer networks. The decomposition temperature (T_d) of the PLO-air-s is around 410 °C while the T_ds of the other polymers were all the same (450 °C). There was no difference in decomposition temperatures between the cross-linked and soluble graft copolymers. Oxidation and cross-linking affected the more thermally stable polymers. When we compare the T_ds of homo PS and homo PMMA at around 350–400 °C, the decomposition temperatures of the graft copolymer of oxidized linseed oil produced higher T_ds. The glass transition temperature (T_g) was found to be 31.7 °C for cross-linked PLO, as indicated in Figure 7. The T_gs of cross-linked and soluble PLO-*graft*-PS graft copolymers were 58.2 °C and 98.5 °C, respectively, while the T_gs of the cross-linked and soluble PLO-*graft*-PMMA graft polymers were 94 °C and 107.4 °C, respectively. The plastization effect of PLO in graft copolymers increased with a rise in the PLO inclusion as well as network formation.

Cell adhesion and spreading on a surface are the processes most effective for assessing the biocompatibility of a synthetic polymer.[17] Figure 8 shows the fibroplast cell adhesion and proliferation on PS and PMMA as controls and PMMA-*graft*-PLO film samples were obtained. There are very few spherical cells at the beginning but in time they proliferate. The spherical cells turn into the shape of out-stretched cells, which can be attributed to the well adhesion of the cells on the surface. Our cell adhesion studies are in progress.

Conclusion

A plant oil and a vinyl monomer were directly copolymerized without the addition of a catalyst or cross-linker such as divinylbenzene, which would more or less inhibit the biodegradability of the end product by the method reported in this paper. As a drying oil, linseed oil produces a mixture of highly branched (soluble) and cross-linked polymeric film via peroxide, hydroperoxide, epoxide and perepoxides in the air or in oxygen flow at room temperature for several weeks. Polymeric linseed oil can initiate the free radical polymerization of vinyl monomers in order to obtain biodegradable synthetic branched graft copolymers. The amount of poly(linseed oil) in the block copolymer structure can be optimized by simply changing the initial ratio of starting materials. PMMA-*graft*-PLO graft copolymer samples can also be used in tissue engineering due to their cell adhesion and development.

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