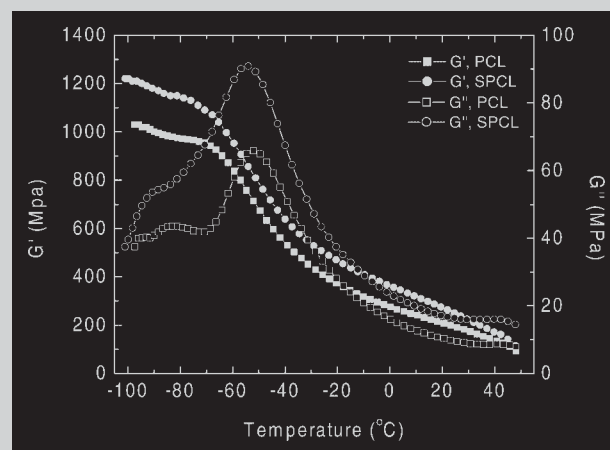


Summary: Polycaprolactone (PCL) and starch/PCL blends (SPCL) are shown to have the potential to be used in a range of biomedical applications and can be processed with conventional melting-based procedures. In this paper, the thermal and thermomechanical analyses of PCL and SPCL were performed, using DSC, optical microscopy and DMA. Starch effectively increased the non-isothermal crystallisation rate of PCL. Non-isothermal crystallisation kinetics was analyzed using Ozawa model, and a method, which combines the theories of Avrami and Ozawa. Starch effectively reinforced PCL and enhanced its damping properties, which indicated that SPCL could be more suitable than PCL in some biomedical applications, as it might help in the dissipation of the mechanical energy generated by the patient movements.



Dynamic mechanical behaviour of PCL and SPCL at 1 Hz.

Thermal and Thermomechanical Behaviour of Polycaprolactone and Starch/Polycaprolactone Blends for Biomedical Applications

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Introduction

Polycaprolactone (PCL) is among the most attractive and commonly used biodegradable polyesters.^[1] It can be used in different biomedical applications,^[2–4] such as in scaffolds in tissue engineering, and for controlled release of drugs. On the other hand, starch is one of the natural biodegradable polymers and is produced at a relatively low price. The development and biodegradable properties of the blends of starch with PCL (SPCL) has been well documented in the literature.^[5–14] Starch helps to lower the cost of the ultimate product as well as to give some biodegradable characteristics to PCL. Recently, SPCL has already been proposed for biomedical applications, including tissue

engineering scaffolds,^[15–17] and for different orthopaedic purposes.^[15,18] Besides adequate physical properties, this blend exhibits good biocompatibility^[16,19] and low inflammatory response.^[20]

Characterising the thermal properties of such systems may be useful for the processing of the material and for the prediction of some features during their potential applications as biomaterials. Non-isothermal crystallisation behaviour is one of the important thermal properties of semi-crystalline polymers to be characterised, since most processing techniques are melt-based and actually occur under non-isothermal conditions, and the resulting physical properties (including mechanical and biodegradable behaviour) are strongly dependent on the morphology formed and

the extent of crystallisation. Examinations concerned with the non-isothermal crystallisation features of PCL and its blends with starch have been published by several authors. For example, Skoglund et al.^[21] presented overall crystallisation characteristics of PCL. Vazquez et al.^[22,23] reported the influence of sisal fibre on the crystallisation behaviour of PCL. However, there is little information concerning the influence of starch on the crystallisation behaviour of PCL. In this article, the melting behaviour and the non-isothermal crystallisation kinetics of typical commercially available PCL and SPCL were studied by DSC. The morphology development upon cooling from the melt was also studied by polarised optical microscopy.

The mechanical characterisation of new polymeric systems is essential to understand their performance under loads and may help to elucidate on the micro-structure of heterogeneous systems, such as semi-crystalline polymers, blends or copolymers. Especially for implanted materials that will withstand mechanical stresses in clinical use (e.g., in vascular or orthopaedic applications), a proper mechanical characterisation is among the most important physical tests that must be carried out. Implantable materials should have a similar mechanical performance of the living tissues that will be in contact with. Most of the biological tissues, possibly excepting dental enamel and echinoderm skeletons, exhibit a time-dependent mechanical behaviour due to their viscoelastic nature. Therefore, it is important to evaluate the solid-state rheological properties of materials aimed at being used in biomedical applications. Dynamic mechanical analysis (DMA) is a thermal analysis technique in which the response of the material under a cyclic load or strain excitation is measured as a function of frequency or temperature, being adequate to probe the viscoelastic properties of polymeric systems.^[24,25] It has also been shown that this technique may be useful to extract relevant information in biomaterials.^[26] A few authors^[5,6,9,27] have shown some DMA data of PCL and SPCL, but they only reported the results at a single frequency; moreover, the data were never integrated in the context of the potential biomedical applications of the materials. In this work DMA was also used to access the thermal properties of the studied materials, especially near glass transition temperature (T_g), and to obtain information about the viscoelastic properties in this temperature region at meaningful frequencies.

Experimental Part

Materials

PCL of commercial grade (TONE[®] 787) was supplied by Union Carbide, with molecular weight 125 000. The blend of corn starch with PCL 30/70 wt.-% (SPCL) was provided by Novamont (Italy). It contained about 63 wt.-% of PCL, 27 wt.-% of corn starch and 10 wt.-% of natural plasticisers. The

molecular weight of PCL presented in SPCL was about 118 000.

Differential Scanning Calorimetry

A Perkin-Elmer DSC 7 was used to study the thermal behaviour of the samples. Sample films of approximately 0.2 mm thickness were obtained by hot-press at 95 °C for several minutes. Samples of about 10 mg were cut from the film. Each sample was used only once and all the runs were carried out under a nitrogen atmosphere.

Three kinds of experiments were performed:

(1) For isothermal crystallisation experiments, the samples were heated to 95 °C at 200 °C · min⁻¹ and held for 5 min to eliminate small residual nuclei that might act as seed crystals. Then, the melt was cooled rapidly to the crystallisation temperature and kept at this temperature for a period of time. After this period, the samples were heated at 10 °C · min⁻¹ without further cooling to characterise the melting behaviour.

(2) In cooling experiments, the samples were heated to 95 °C at 200 °C · min⁻¹ and held for 5 min. Then, the melt was cooled to crystallise at selected constant cooling rates, ranging from 2.5 to 40 °C · min⁻¹.

(3) To investigate the glass transition characteristics, the samples were heated to 95 °C at 200 °C · min⁻¹ and held for 5 min. Then, the melt was cooled rapidly to -80 °C, and the heat flow was recorded during a heating at 10 °C · min⁻¹.

Separate calibrations for baseline were made for all heating and cooling rates. Calibration for the temperature and energy scale was carried out using a pure indium standard. Precautions were taken for temperature calibration on cooling. 4-Cyano-4'-octyloxy-biphenyl (M24), which was kindly supplied by Prof. Schick (University of Rostock, Germany), was used. The calibration was performed following the procedure suggested in the literature.^[28]

Optical Microscopy

Non-isothermal crystallisation experiments were conducted on the thin films of the polymers between microscope glass slides placed on a Mettler hot-stage (FP80) and an Olympus BH-2 polarising microscope, equipped with a video camera system. The samples were heated to 95 °C, maintained for 5 min and then cooled down at 2 °C · min⁻¹.

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) testing was carried out using a Mettler DMA861 equipment. The samples were obtained by compression moulding at a constant force of 10 tons at 65 °C for 20 min and then cut into bars of about 5.5 × 3 × 1 mm³. The testing configuration was shear. A constant dynamic force of 10 N was applied and six different frequencies were used (1, 5, 10, 20, 50 and 100 Hz). The characterisation of the glass transition was carried out by the tests performed in the temperature range of -102 to 50 °C at a heating rate of 5 °C · min⁻¹.

Results and Discussion

Melting Behaviour

The investigation of the melting characteristics is helpful for the determination of the processing parameters of the studied systems. Figure 1(A) and (B) shows the melting behaviour of PCL and SPCL upon heating at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, immediately after being crystallised isothermally at four different temperatures from 20 to $40\text{ }^{\circ}\text{C}$, for 30 or 60 min. It can be seen that crystallisation temperature has a significant effect on the melting behaviour of PCL and SPCL. With increasing isothermal crystallisation temperature, the melting peak moves to higher temperature for both PCL and SPCL. The melting peaks of PCL are broader than those of SPCL.

Table 1 summarises characteristic data for melting behaviour of PCL and SPCL. At the same isothermal cry-

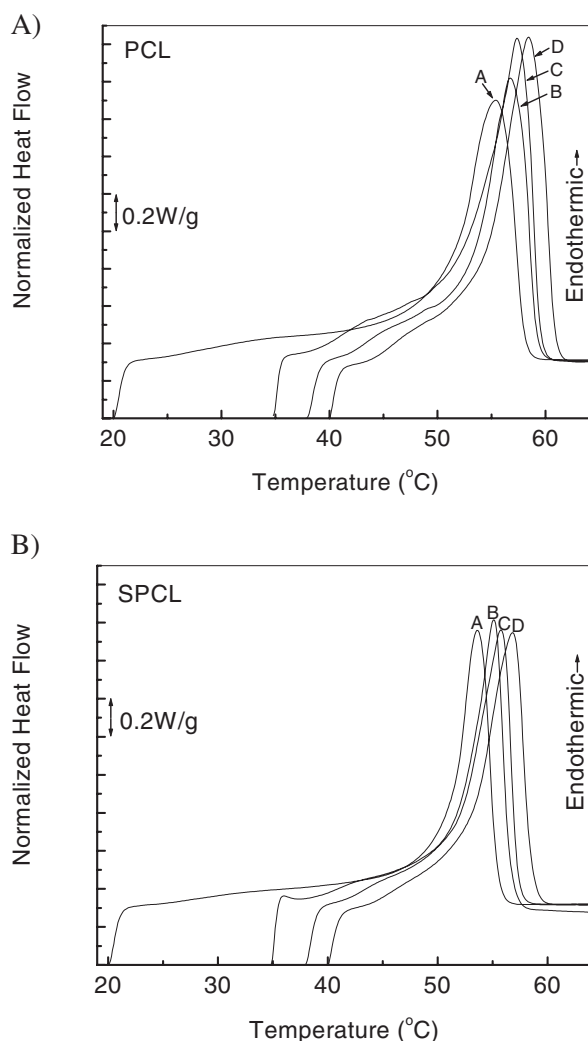


Figure 1. DSC melting thermograms of PCL and SPCL upon heating at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ after being crystallised isothermally under various conditions. (A) $20\text{ }^{\circ}\text{C}$ for 60 min, (B) $35\text{ }^{\circ}\text{C}$ for 30 min, (C) $38\text{ }^{\circ}\text{C}$ for 30 min, (D) $40\text{ }^{\circ}\text{C}$ for 60 min.

Table 1. Melting behaviour of PCL and SPCL probed by DSC.

Crystallisation conditions	$20\text{ }^{\circ}\text{C}$, 60 min	$35\text{ }^{\circ}\text{C}$, 30 min	$38\text{ }^{\circ}\text{C}$, 30 min	$40\text{ }^{\circ}\text{C}$, 60 min
PCL				
$T_m/{}^{\circ}\text{C}$	55.3	56.7	57.3	58.4
$\Delta H_f/(\text{J}\cdot\text{g}^{-1})$	63.3	61.3	59.8	59.8
Crystallinity/%	45.4	43.9	42.9	42.9
SPCL				
$T_m/{}^{\circ}\text{C}$	53.6	55.1	55.7	56.8
$\Delta H_f/(\text{J}\cdot\text{g}^{-1})^{\text{a}}$	43.3	41.5	41.6	41.8
Crystallinity/% ^{b)}	49.3	47.2	47.3	47.6

a) Per gram of total sample.

b) Based on unit mass of PCL component.

stallisation condition, the subsequent melting peak temperature, T_m , for PCL is about $1.6\text{ }^{\circ}\text{C}$ higher than that of SPCL. For each of PCL and SPCL, the melting enthalpy, ΔH_f , is insensitive to isothermal crystallisation conditions at the studied range. For PCL $\Delta H_f = 61.1 \pm 1.3\text{ J}\cdot\text{g}^{-1}$, and for SPCL $\Delta H_f = 42.1 \pm 0.7\text{ J}\cdot\text{g}^{-1}$. The values of ΔH_f can be compared with $139.5\text{ J}\cdot\text{g}^{-1}$, corresponding to a 100% crystalline PCL.^[29] Follow this, the crystallinity of PCL can be easily estimated. The crystallinity is $43.8 \pm 0.9\%$ and $47.9 \pm 0.8\%$ for PCL and for PCL within SPCL, respectively.

It is well known that plasticiser can decrease the melting point of polymers.^[30] As mentioned earlier, SPCL contains about 10% of natural plasticiser, while the molecular weight of PCL and that of SPCL are very close. Therefore, it is reasonable to suggest that the difference in the melting temperature is probably due to the plasticisation effect of the plasticiser on PCL. Another possibility is that the existence of starch and plasticiser in SPCL leads to the difference of crystal lamellae between SPCL and PCL.

Non-Isothermal Crystallisation Behaviour

Figure 2 presents the non-isothermal crystallisation peaks recorded at different cooling rates. As expected, with increasing cooling rate, the exothermic trace becomes wider and shifts towards lower temperatures. The observation is general for both PCL and SPCL samples.

Table 2 summarises the main features for non-isothermal crystallisation of PCL and SPCL. For both PCL and SPCL, the crystallisation peak temperatures, T_c , move towards lower temperature with increasing cooling rate. For a given cooling rate, the T_c value for SPCL is higher than that for PCL. The difference in T_c , at cooling rate from 2.5 to $40\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, is $21.1\text{ }^{\circ}\text{C}$ for PCL and $10.5\text{ }^{\circ}\text{C}$ for SPCL, respectively. For both PCL and SPCL, the crystallisation enthalpies, ΔH_c , and their crystallinities are insensitive to cooling rates at the studied range, which is consistent with the results for PCL reported by Skoglund et al.^[21] By comparing ΔH_c with $139.5\text{ J}\cdot\text{g}^{-1}$, for a 100% crystalline PCL, the obtained crystallinity is $38.2 \pm 0.4\%$ and

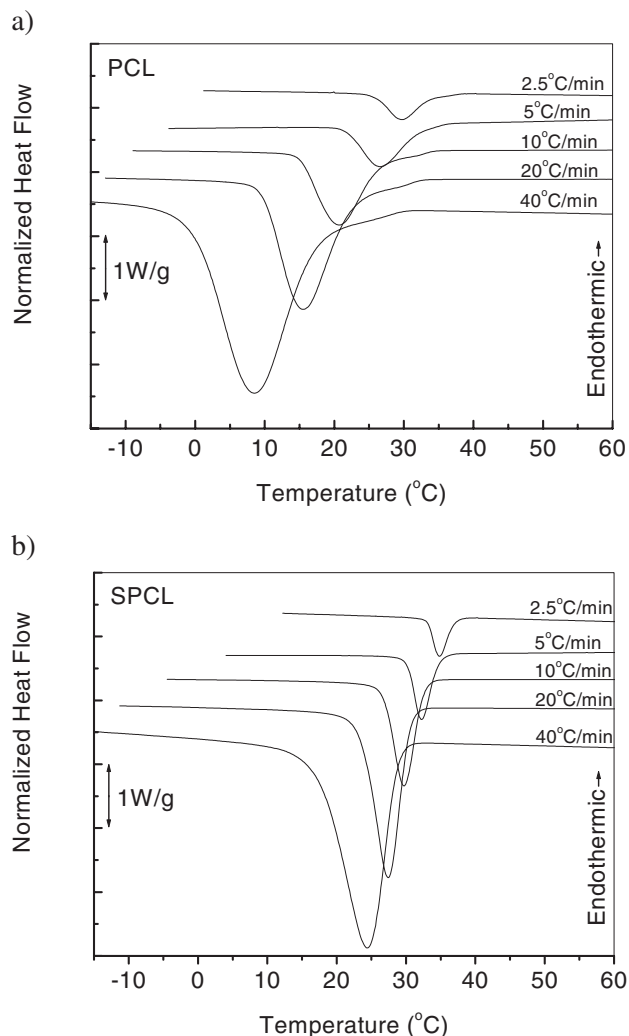


Figure 2. Non-isothermal crystallisation exotherms of (a) PCL and (b) SPCL at five different cooling rates.

Table 2. Non-isothermal crystallisation behaviour of PCL and SPCL studied by DSC.

Sample	ϕ	T_c	$\Delta H_c^{(a)}$	Crystallinity ^{b)}	$t_{1/2}$
	$^{\circ}\text{C} \cdot \text{min}^{-1}$	$^{\circ}\text{C}$	J/g	%	min
PCL	2.5	29.7	54.4	39.0	3.55
	5	26.7	52.4	37.5	2.02
	10	20.6	53.6	38.4	1.35
	20	15.5	53.0	38.0	0.82
	40	8.6	53.0	38.0	0.54
SPCL	2.5	34.9	36.3	41.3	1.68
	5	32.3	35.8	40.7	1.00
	10	29.7	36.6	41.6	0.53
	20	27.4	35.6	40.5	0.29
	40	24.4	35.2	40.1	0.19

^{a)} Per gram of total sample.

^{b)} Based on unit mass of PCL component.

$40.8 \pm 0.5\%$ for PCL and for PCL within SPCL, respectively. The last column ($t_{1/2}$) of Table 2 is the half-time of crystallisation and it will be discussed further in the next section.

To further understand the non-isothermal crystallisation behaviour, it is necessary to present the data of relative crystallinity $X(T)$, as a function of crystallisation temperature T , or $X(t)$, as a function of crystallisation time t . $X(T)$ can be formulated as^[31]

$$X(T) = \frac{\int_{T_0}^T \left(\frac{dH_c}{dT}\right) dT}{\int_{T_0}^{T_{\infty}} \left(\frac{dH_c}{dT}\right) dT} \quad (1)$$

where T_0 and T_{∞} represent the crystallisation onset and end temperature, respectively, and dH_c is the enthalpy of crystallisation released during an infinitesimal temperature range dT . The horizontal temperature scale can be transformed into time domain using the following relationship:

$$t = (T_0 - T)/\phi \quad (2)$$

where T is the temperature at crystallization time t , and ϕ is the cooling rate.

An important parameter which can be obtained is the half-time of crystallisation $t_{1/2}$, which is the change in time from the onset of crystallisation to the time at which $X(t)$ is 50%. It can be seen that from Table 2, for PCL and SPCL, the higher the cooling rate, the shorter is the time for completing the crystallisation. At each cooling rate, the crystallisation rate of SPCL is much faster than that of pure PCL. This suggests that starch in SPCL acts as nucleating agent, which could enhance the crystallisation rate of PCL.^[6] It has also been reported that starch could effectively increase the crystallisation rate of poly(lactic acid), even at a 1% content.^[32]

The method developed by Dobreva-Velva and Gutzow^[33] was also applied to analyse the non-isothermal crystallisation behaviour of polymers in the presence of nucleation agents. The relationship is established as the following:

$$\log \phi = \text{const.} - B/(T_m - T_c)^2 \quad (3)$$

The activity of the filler is related to the parameter ϕ :

$$\phi = B^*/B^0 \quad (4)$$

where B^* is the value of B when the polymer is filled and B^0 when it is unfilled.

The value of ϕ decreases from 1 to 0 as the polymer crystallises in the presence of more efficient nucleating particles. This approach has been successfully applied to evaluate the nucleating rate of PP filled with different mineral particles.^[34–36]

In this paper the value of ϕ obtained for starch in PCL was 0.65 (graphics with the fits not shown), which is appreciable

and comparable to the value found in PP-Talc composites, or PP-aluminium hydroxide composites.^[34–36]

The crystallisation kinetics of PCL and SPCL will be now discussed. Several methods to analyse non-isothermal crystallisation kinetics have been developed.^[37–39] Ozawa explained the effect of the cooling rate on the non-isothermal crystallisation by modifying the Avrami equation, assuming that crystallisation occurs at a constant cooling rate ϕ .^[37] According to Ozawa's theory, the relative crystallinity at temperature T , $X(T)$, can be calculated from the following equation:

$$1 - X(T) = \exp[-K(T)/\phi^m] \quad (5)$$

where $K(T)$ is the Ozawa crystallisation rate constant, and m is the Ozawa exponent that depends on the dimension of crystal growth. Taking the double-logarithmic form,

$$\log\{-\ln[1 - X(T)]\} = \log K(T) - m \log \phi \quad (6)$$

and plotting $\log\{-\ln[1 - X(T)]\}$ against $\log \phi$ at a given temperature, a straight line should be obtained if the Ozawa method is valid. The Ozawa crystallisation rate constant $K(T)$ is taken as the antilogarithmic value of the y-intercept, and the Ozawa exponent m is taken as the negative value of the slope.

Figure 3 illustrates such plots for the non-isothermal crystallisation data of PCL and SPCL, using a series of temperatures. For PCL, the values of m and $K(T)$, in the temperature range of 20–33 °C, are summarised in Table 3. Within the studied temperature range, the values of m are almost constant. It can be concluded that the Ozawa approach could satisfyingly describe the non-isothermal crystallisation kinetics of PCL. The average value of m obtained in this study is equal to 2.3 ± 0.1 , which is lower than the values, from 2.9 to 3.6, reported by Skoglund et al.^[21] The Ozawa rate constant $K(T)$ is found to decrease with increasing temperature, suggesting that PCL crystallises slower with increasing temperature. For SPCL, the general curvature seen in Figure 3 makes impossible to determine m and $K(T)$. It is apparent that the Ozawa analysis cannot adequately describe the non-isothermal crystallisation kinetics of SPCL, probably because of the disregarded assumptions in Ozawa theory, where, for instance, the secondary crystallisation was not considered. Wang et al.^[40] have also reported that the Ozawa approach could describe the non-isothermal crystallisation for poly(ethylene terephthalate) (PET), but not for PET/clay nanocomposites.

Liu et al.^[38] developed a method to describe the non-isothermal crystallisation by combining the Ozawa and Avrami equations. For the non-isothermal crystallisation

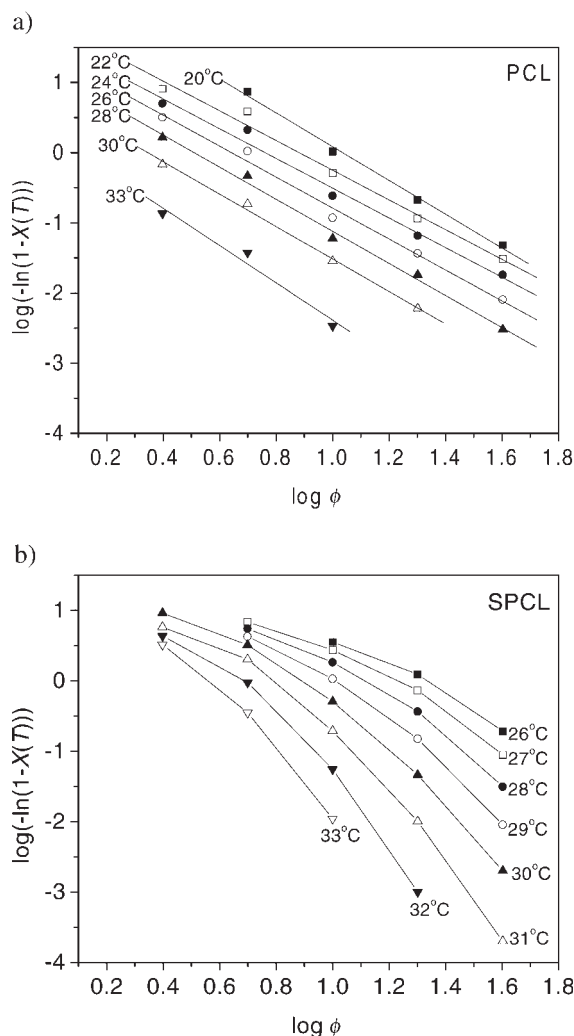


Figure 3. Ozawa plots of $\log\{-\ln[1 - X(T)]\}$ versus $\log \phi$ for crystallisation of (a) PCL and (b) SPCL.

process, the main physical variables related to the process are the relative degree of crystallinity $X(t)$, cooling rate ϕ and crystallisation temperature T . Both the Ozawa and Avrami equations can relate these variables as follows:

$$\log Z + n \log t = \log K(T) - m \log \phi \quad (7)$$

and by rearrangement, its final form is given as below:

$$\log \phi = \log F(T) - a \log t \quad (8)$$

where the kinetic parameter, $F(T) = [K(T)/Z]^{1/m}$, refers to the value of cooling rate chosen at unit crystallisation time when the system has a defined degree of crystallinity, and a is the ratio of the Avrami exponent n to the Ozawa exponent

Table 3. Non-isothermal crystallisation kinetic parameters for PCL based on the Ozawa equation.

$T/^\circ\text{C}$	20	22	24	26	28	30	33
m	2.4	2.3	2.1	2.2	2.3	2.3	2.7
$K(T)$	3.13×10^2	1.32×10^2	4.11×10^1	2.62×10^1	1.47×10^1	6.30	1.87

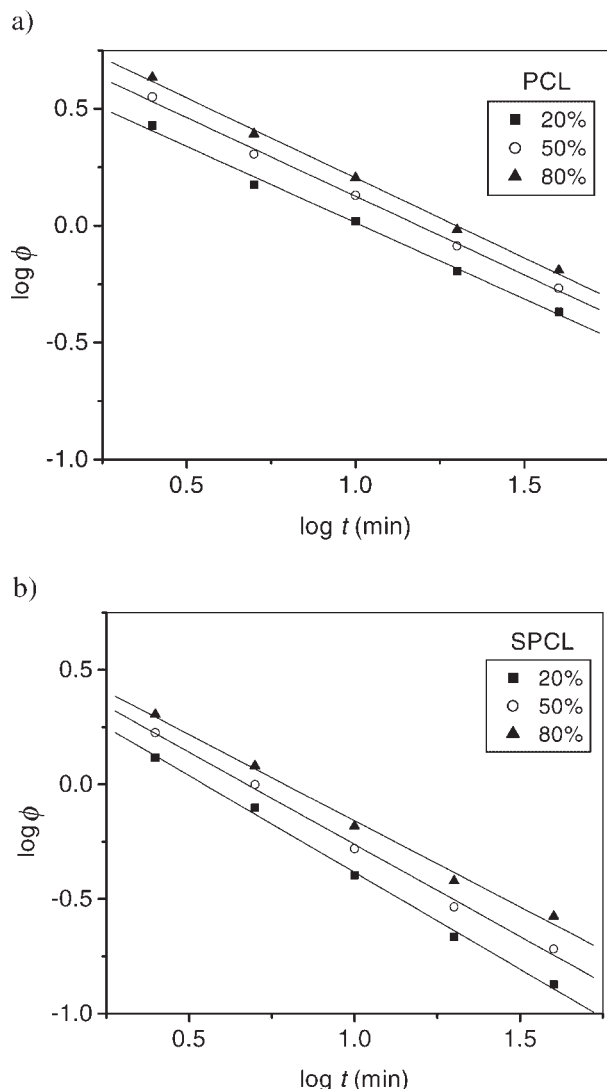


Figure 4. Plots of $\log \phi$ versus $\log t$ for (a) PCL and (b) SPCL.

m (i.e. $a = n/m$). At a given degree of crystallinity, by plotting $\log \phi$ versus $\log t$ (Figure 4), the values of a and $F(T)$ could be obtained by the slopes and the intercepts of these lines, respectively (Table 4). The values of $F(T)$ systematically increase with increasing relative crystallinity for PCL and SPCL. This means that, at a defined crystallisation time, a higher cooling rate should be used to obtain a higher degree of crystallinity. The values of a are

Table 4. Non-isothermal crystallisation kinetic parameters based on the combination of the Avrami-Ozawa equations.

$X(t)/\%$	20	50	80
PCL			
$F(T)$	4.63	6.29	7.74
a	0.65	0.67	0.68
SPCL			
$F(T)$	2.89	3.49	3.92
a	0.84	0.80	0.75

almost constant for each sample, varying between 0.65 and 0.68 for PCL, and between 0.75 and 0.84 for SPCL. It is clear that this combined method is adequate in describing the non-isothermal process of PCL and SPCL, which was found to be also valid for both PET and its composites with clay,^[40,41] and poly(ethylene 2,6-naphthalate) and its composites with silica.^[42]

The optical micrographs of PCL and SPCL upon cooling from the melt are shown in Figure 5. It can be seen that SPCL starts to crystallise at higher temperature than PCL, and the crystallisation rate of SPCL is higher than that of PCL, which are consistent with the observation from DSC. It can also be observed that the concentration of spherulites of SPCL is much higher than that of PCL, and the sizes of spherulites of SPCL are smaller than that of PCL. It may be then concluded that starch can effectively influence the crystallisation development of PCL and change the kinetics, the extent of crystallisation and the spherulitic morphology.

Dynamic Mechanical Analysis

In typical DMA experiments it is possible to measure, as a function of temperature or frequency, both the elastic, G' , and viscous (loss) component, G'' , of the complex modulus: $G^* = G' + iG''$. The damping properties of the material may be accessed through the loss factor: $\tan \delta = G''/G'$. Figure 6 and 7 show the elastic shear modulus and loss shear modulus of the two materials under study. The upper temperature limit was dictated by the melting process, which was already analysed by DSC. The glass transition process of both materials is detected as a sudden decrease of the complex modulus and as a peak in the loss curve. The temperatures of the glass transition measured in the maximum of G'' are given in Table 5 for the different frequencies used.

Figure 8 shows the relaxation map for the two studied materials using the data of Table 5. The two trends seem to converge at lower frequencies. This is consistent with the similar glass transition found for the two materials by DSC: -64.3°C for PCL and -64.6°C for SPCL (at heating rate: $10^\circ\text{C}\cdot\text{min}^{-1}$) (results are not shown). Such values are similar to the value of $T_g = -66.4^\circ\text{C}$ for a similar blend reported elsewhere.^[43] Within the frequency range used for the DMA experiments, it is not clear in the plots of Figure 8 the expected curvature in the $\log f$ versus $1/T$ plot due to the so-called WLF behaviour.^[24,25] Therefore, the data were fitted according to a simple Arrhenius model. The apparent activation energy, E_a , is slightly higher for the SPCL material ($150\text{ kJ}\cdot\text{mol}^{-1}$) compared to that of the PCL material ($123\text{ kJ}\cdot\text{mol}^{-1}$). As the glass transition temperatures of the two materials are similar, the difference in the apparent activation energy reflects differences in the so-called fragility. The classification of liquids as "strong" and "fragile" has been promoted by Angell to describe the relaxation in glass-forming systems.^[43] One relevant parameter

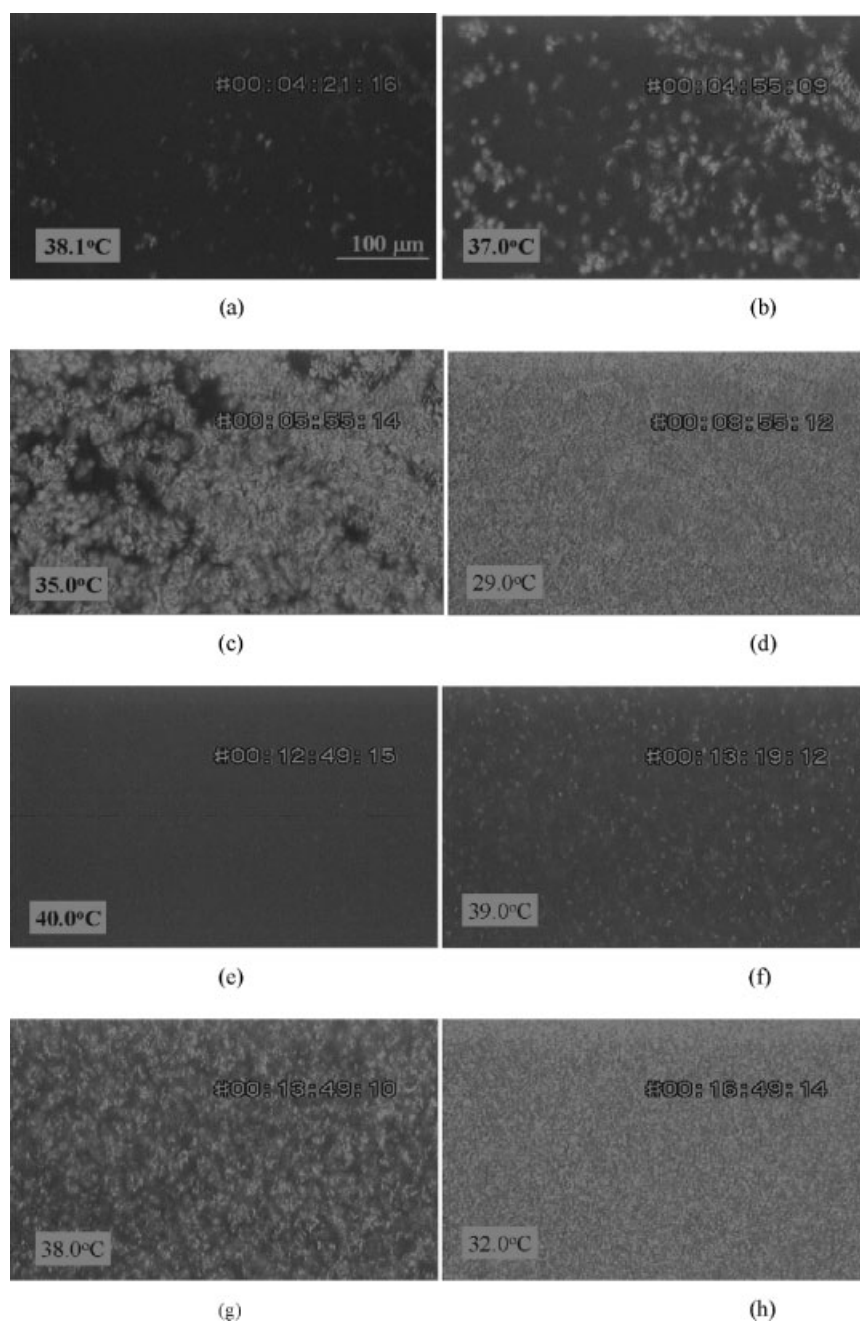


Figure 5. Polarised optical micrographs of PCL and SPCL during cooling at $2\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ from the melt ($95\text{ }^{\circ}\text{C}$). Images (a)–(d) are for PCL and images (e)–(h) are for SPCL.

here is the fragility index m that is related to the rate at which the characteristic time, or other related property such as viscosity, decreases with increasing temperature at T_g , when plotted on a normalised T_g/T plot.^[44,45] From the differences observed in E_a we may conclude that PCL is more “strong” than SPCL. From a practical point of view, this would mean that around and above T_g , the change of dynamic properties in SPCL with temperature should be more smooth than that in PCL, which is consistent with the presence of the starch phase.

On the other hand, the slightly lower values of T_g in the SPCL material could be due to both the plasticiser content and/or the higher crystallisation rate in this polymeric system, which could induce an amorphous phase of higher mobility. This kind of result has been previously reported for PP-talc composites.^[34–36] In these materials the talc phase also acted as nucleating agent for the polymer.

The values of G' give relevant indications on the stiffness properties of the materials. Below T_g the values are above 1 GPa which is typical for glassy polymers. The storage

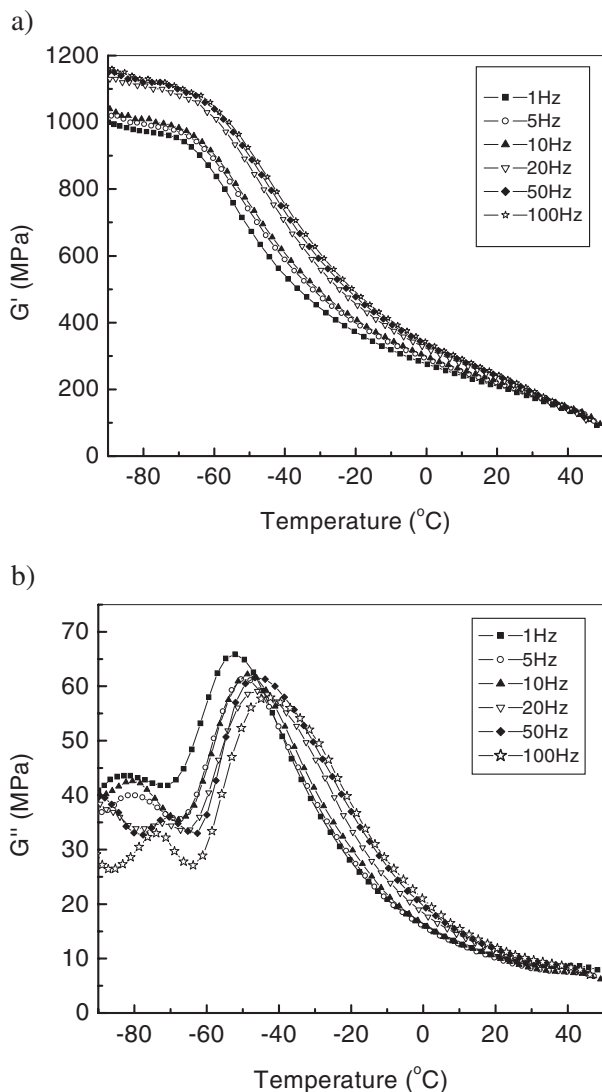


Figure 6. Dynamic mechanical behaviour of PCL at different frequencies. (a) Elastic shear modulus and (b) loss modulus.

modulus is higher for SPCL than for PCL throughout the temperature range analysed, indicating that starch has a reinforcing effect in this polyester. Essentially, the temperature variation of G' is similar to the storage modulus measured by three-point bending as a function of temperature, reported elsewhere.^[26] The values of G' at 37 °C are important if one pretends to use such systems in biomedical applications. Those are shown in Table 5 for the two studied materials and for the different frequencies analysed.

The values of the loss factor at 37 °C do not depend significantly on frequency for the two materials. For PCL $\tan \delta = 0.05 \pm 0.01$ and for SPCL $\tan \delta = 0.08 \pm 0.01$. Therefore, such materials exhibit considerable damping capability that may be useful, for example, in some medical

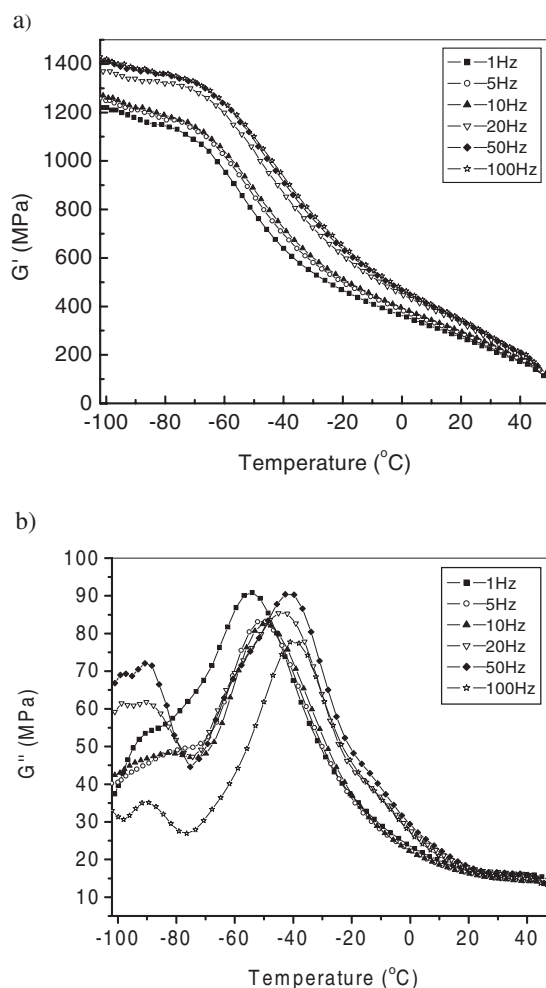


Figure 7. Dynamic mechanical behaviour of SPCL at different frequencies. (a) Elastic shear modulus and (b) loss modulus.

applications: for orthopaedic purposes the implanted material should have significant values of $\tan \delta$ because bone also exhibits clear viscoelastic behaviour, with $\tan \delta$ ranging between 0.02 and 0.03 at meaningfully frequencies.^[46]

Table 5. Temperature of maximum of G'' for the α -relaxation and storage modulus at 37 °C for PCL and SPCL, obtained by DMA.

Frequency Hz	PCL		SPCL	
	$T_{\max, G''}$ °C	G' (37 °C) MPa	$T_{\max, G''}$ °C	G' (37 °C) MPa
1	-45.5	144	-48.5	186
5	-42.0	154	-43.5	204
10	-39.8	161	-41.9	201
20	-35.1	138	-39.1	193
50	-33.1	146	-36.8	206
100	-28.9	145	-35.1	215

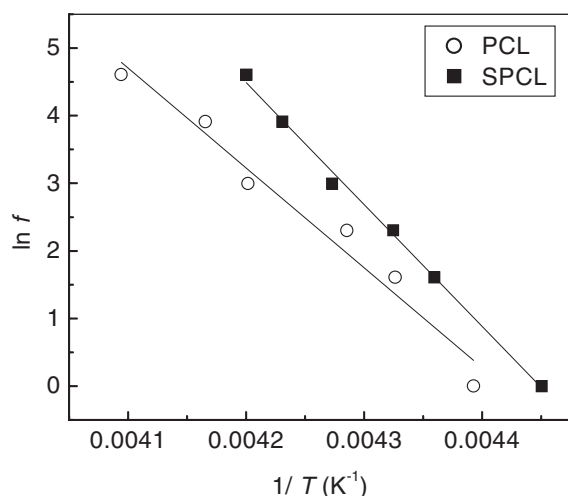


Figure 8. Relaxation plot for PCL (circles) and SPCL (squares) with the corresponding Arrhenius fits.

Conclusion

We reported a comparative study on the melting, non-isothermal crystallisation and thermomechanical behaviour for typical commercial available PCL and the blend of starch with PCL 30/70 wt.-% (SPCL), using DSC, optical microscopy and DMA.

The melting peak temperature and melting enthalpy for PCL are higher than those of SPCL.

Non-isothermal crystallisation investigations show that the crystallisation rate of SPCL is much higher than that of PCL, indicating that starch acts as an effective nucleation agent for PCL. The crystallinity of PCL within SPCL, obtained after cooling from the melt, is larger than that of pure PCL. For both PCL and SPCL, the crystallinities obtained are insensitive to cooling rates at the studied range from 2.5 to 40 °C · min⁻¹. The concentration of spherulites of SPCL is much higher than that of PCL and the sizes of spherulites of SPCL are smaller than that of PCL. Crystallisation kinetics analysis shows that the Ozawa model can well describe the non-isothermal crystallisation of PCL, but fails to describe that of SPCL. However, the method developed by Liu et al., which combines the theories of Avrami and Ozawa, is adequate in describing the non-isothermal crystallisation of PCL and SPCL.

Both DSC and DMA results show that the T_g is higher for PCL than for SPCL. The change of the dynamic T_g with frequency is more pronounced for PCL, the apparent activation energy at T_g being higher for SPCL. The temperature dependence of G' shows that starch has an effective reinforcement effect in PCL. At 37 °C, both materials exhibit interesting damping properties (especially SPCL), which may be relevant in orthopaedic applications, as it may help in the dissipation of the mechanical energy generated by the patient movements.

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