Thermomechanical behavior and nonisothermal crystallization kinetics of poly(ε-caprolactone) and poly(ε-caprolactone)/poly(N-vinylpyrrolidone) blends

Zhimin Xing,1∗ Liusheng Zha,1,2 Guisheng Yang3

1 State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai, 201620; e-mail: zhiminxinghxs@126.com
2 Research Center for Analysis and Measurement, Donghua University, Shanghai, 201620; e-mail: lszha@dhu.edu.cn.
3 Shanghai Genius Advanced Materials Co., Ltd, Shanghai, China; 201109; e-mail: ygs@geniuscn.com

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Abstract: Poly(ε-caprolactone) (PCL) and PCL/Poly(N-vinylpyrrolidone) (PVP) blends are shown to have the potential to be used in a range of biomedical applications and can be processed with successive in-situ polymerization procedures. In this paper, the thermomechanical analysis of PCL and PCL/PVP blends was performed using dynamic mechanical analysis (DMA). The storage and loss moduli as a function of temperature and frequency were recorded. The nonisothermal crystallization kinetics of PCL and PCL/PVP blends were analyzed using Ozawa model and Mo–Liu equation, a combination equation of Avrami and Ozawa formulas. The Ozawa analysis failed to describe the nonisothermal crystallization behavior of blends, whereas the Mo–Liu equation successfully described the nonisothermal crystallization kinetics of PCL and PCL/PVP blends. In addition, the value of crystallization rate coefficient under nonisothermal crystallization conditions was calculated. The PCL/PVP blends compared with the pure PCL and PVP had a restrain effect on the crystallization kinetics of PCL in the blends. Combining the results of DMA and DSC, PVP effectively decreased the crystallinity of PCL and enhanced its damping properties, which indicated that PCL/PVP blends 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.

Introduction

Polymer blending has gained considerable interest, since it constitutes an economical alternative to synthesizing new monomers in the development of new materials with improved properties. PCL is among the most attractive and commonly used biodegradable polyesters due to its biodegradability, favourable miscibility with other polymers, and low temperature adhesiveness. It can be used in different biomedical applications, such as in scaffolds, tissue engineering, and for controlled release of drugs [1-4]. By now, many researchers have synthesized PCL copolymers or blends such as PCL/PEG [5], PCL/polysaccharides [6-8], PCL/PVC [9], as well as incorporated various functional groups into PCL [10, 11]. Even some PCL-based organic-inorganic hybrid materials have also been synthesized by sol-gel method [12]. Based on successive in-situ polymerization method, we successfully prepared polycaprolactone/poly(N-vinylpyrrolidone) (PCL/PVP) blends [13]. PVP is considered a biocompatible and biodegradable material, can replace PEO as a food thickener,
has relatively fast hydrolytic degradation and can preserve platelet functions when the platelets contact the polymer surfaces [14, 15]. So, the PCL/PVP blends which combine the properties of PCL and PVP might be more suitable than PCL in some biomedical applications. However, there is little information concerning the influence of PVP on crystallization or thermomechanical behavior of PCL.

Characterizing of the mechanical properties of new polymeric systems is essential to understand their performance under loads and may help to elucidate on the microstructure of heterogeneous systems, such as semicrystalline polymers, blends or copolymers. Especially for implanted materials that should withstand mechanical stresses in clinical use, such as in vascular or orthopaedic applications, a proper mechanical characterization 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 the materials aimed to be used in biomedical applications. Dynamic mechanical analysis (DMA) is a 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 test plastic and viscoelastic properties of polymeric systems [16-18]. It has also been shown that this technique may be useful to extract relevant information on biomaterials [19]. The DMA is much more sensitive than differential scanning calorimetry (DSC) or thermomechanical analysis (TMA) and these techniques can easily measure transitions not apparent in other thermal methods [20]. This sensitivity allows DMA to detect glass transition temperature $T_g$ of highly crosslinked thermosets or of thin coatings. Recently, the use of a material pocket allows one to extend this sensitivity even to powders [21]. In this work, DMA data of PCL and PCL/PVP blends were integrated in the context of the potential biomedical applications. Moreover, they were also used to access thermal properties of the studied materials, especially near $T_g$, and to obtain information about viscoelastic properties in this temperature region at meaningful frequencies.

The thermal characterization of such systems may be useful for the processing of the material and for prediction of some features during their potential applications as biomaterials. Nonisothermal crystallization behaviour is one of the important thermal properties of semicrystalline polymers to be characterized, since most processing techniques are melt-based and actually occur under nonisothermal conditions, and the resulting physical properties (including mechanical and biodegradable behaviour) are strongly dependent on the morphology formed and the extent of crystallization. Examinations concerning nonisothermal crystallization of PCL and its blends have been published by several authors. Skoglund et al. [22] presented overall crystallization characteristics of PCL. Vazquez et al. [23, 24] reported the influence of sisal fiber on the crystallization behavior of PCL. Mano et al. [25] analyzed kinetics of nonisothermal crystallization of starch/PCL blends. In our article, the nonisothermal crystallization kinetics of PCL and PCL/PVP blends all synthesized in the lab were studied by DSC.

Results and discussion

Dynamic Mechanical Analysis

In typical DMA experiments it is possible to measure, as a function of temperature or frequency, both the elastic, $E'$, and viscous (loss) component, $E''$, of the complex
modulus: $E'' = E' + iE''$. The damping properties of the material may be acceded through the loss factor: $\tan \delta = E'' / E'$. Figures 2, 3 and 4 show the above properties of PCL and PCL/PVP blends (V10, V20) at 1 Hz. The upper temperature limit was dictated by the melting process, which was already analyzed by DSC. The glass transition is detected as a sudden decrease of the complex modulus and as a peak in the loss curve.

![Synthetic scheme showing the PCL/PVP blends preparation.](image)

**Fig. 1.** Synthetic scheme showing the PCL/PVP blends preparation.

![Storage modulus of PCL, and V10, V20 blends vs. temperature at 1 Hz.](image)

**Fig. 2.** Storage modulus of PCL, and V10, V20 blends vs. temperature at 1 Hz.
The values of $E'$ in Figure 2 give relevant indications on the stiffness properties of the materials. Below $T_g$, the $E'$ values are above 1 GPa what is typical for glassy polymers [25]. The storage modulus is higher for PCL/PVP blends than for PCL throughout the analyzed temperature range, indicating that PVP has a reinforcing effect in this system. Figure 3 shows the loss modulus of PCL and the PCL/PVP blends. In this Figure, the glass transition exhibits as a peak at around -60 °C. The loss factor is shown in Figure 4. The Figures 5 and 6 show the dynamic behaviour of PCL and V10 blend at different frequencies. The values of $E'$ at 37 °C are important if one pretends to use such systems in biomedical applications. Digital values of the mechanical parameters at 37°C and different frequencies are listed in Table 1.
Tab. 1. Storage modulus and loss factor of PCL and the PCL/PVP V10 blend at 37 °C obtained by DMA.

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>PCL</th>
<th>PCL/PVP blend (V10)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E' (MPa)</td>
<td>tanδ</td>
</tr>
<tr>
<td>1</td>
<td>311</td>
<td>0.079</td>
</tr>
<tr>
<td>5</td>
<td>319</td>
<td>0.078</td>
</tr>
<tr>
<td>10</td>
<td>339</td>
<td>0.084</td>
</tr>
<tr>
<td>50</td>
<td>337</td>
<td>0.087</td>
</tr>
<tr>
<td>100</td>
<td>315</td>
<td>0.081</td>
</tr>
</tbody>
</table>

Fig. 5. Storage modulus of PCL (a) and V10 blend (b) vs. temperature at different frequencies.

Fig. 6. Loss modulus of PCL (a) and V10 blend (b) vs. temperature at different frequencies.

From the Table 1, we can figure out that the values of the loss factor at 37 °C do not depend significantly on frequency for the two materials. For PCL and the PCL/PVP
blend, both tan δ values remain near to 0.08. One can say, that such materials exhibit considerable damping capability useful in some medical applications, for example for orthopaedic purposes where the implanted material should have significant values of tan δ because bone also exhibits viscoelastic behaviour with tan δ ranging between 0.02 and 0.03 at meaningful frequencies [26].

![Graph](image)

**Fig. 7.** Frequency vs. inverse temperature for PCL and V10 blend with corresponding Arrhenius fit.

Figure 7 shows the relaxation plot for the two studied materials. It is clear from the plots shown in the figure that within the frequency f range used in the DMA experiments, the curvature of $ln f$ versus $1/T$ fits the simple Arrhenius model, $ln f=lnA-Ea/RT$. The apparent activation energy $Ea$ is slightly higher for the V10 blend (127 kJ/mol) compared to that of pure PCL (115 kJ/mol). PCL and V10 blend have similar glass transition temperature, especially at lower frequencies. Unlike the definition of brittleness developed using the DMA in conjunction with the ultimate strength of the material measured as the strain at break [27], 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. Classification of liquids as “strong” and “fragile” has been promoted by Angell to describe the relaxation in glass-forming systems [28]. One relevant parameter 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 when plotted vs. $T_g/T$ [29, 30]. From the differences in $Ea$ we may conclude that PCL is more “strong” than the PCL/PVP blends. From a practical point of view, this would mean that the change of dynamic properties in PCL/PVP blends with temperature around and above $T_g$ should be smoother than that in PCL, which is consistent with the presence of the PVP phase.

**Nonisothermal crystallization behaviour**

In processing, such as extrusion, injection molding, and film production, crystallization usually proceeds under dynamic nonisothermal conditions. So, it is of practical significance to study the crystallization kinetics under nonisothermal conditions. The nonisothermal crystallization exothermic curves of PCL and the PCL/PVP blends at various cooling rates ($R$) are shown in Figure 8. $T_c$ is the peak
temperature at which the crystallization rate is maximum, and $T_c$ shifts to a lower values with increasing cooling rate. When the polymer was undergoing crystallization at a lower cooling rate, it had a relatively long time remaining within the temperature range that promoted sufficient mobility of segments for the growth of crystallites, but when cooled at a relatively high rate, however, the segments were frozen before crystallite formation, thereby decreasing $T_c$. The values of $T_c$, crystallization enthalpy $\Delta H_c$ at different cooling rates, and the crystallinity degree determined with the $\Delta H_c$ value of 139.5 J/g for 100% crystalline PCL [31], as well as crystallization half-time are listed in Table 2.

![Fig. 8](image)

**Fig. 8.** Heat flow vs. temperature during nonisothermal crystallization of PCL and PCL/PVP blends at different cooling rates by DSC.

**Tab. 2.** Non-isothermal crystallization behaviour of PCL and PCL/PVP blends studied by DSC.

<table>
<thead>
<tr>
<th>Samples</th>
<th>R</th>
<th>$T_c$</th>
<th>$\Delta H_c$</th>
<th>Crystallinity</th>
<th>$t_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^\circ C$/min</td>
<td>$^\circ C$</td>
<td>J/g</td>
<td>$%$</td>
<td>min</td>
</tr>
<tr>
<td>PCL</td>
<td>2.5</td>
<td>39.8</td>
<td>58.8</td>
<td>42.2</td>
<td>2.23</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>38.4</td>
<td>60.9</td>
<td>43.7</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>36.8</td>
<td>67.8</td>
<td>48.6</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>33.9</td>
<td>64.8</td>
<td>46.5</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>29.2</td>
<td>61.4</td>
<td>44.0</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>39.1</td>
<td>57.8</td>
<td>46.0</td>
<td>2.96</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>37.4</td>
<td>57.9</td>
<td>46.1</td>
<td>2.18</td>
</tr>
<tr>
<td>V10</td>
<td>10</td>
<td>35.1</td>
<td>56.4</td>
<td>44.9</td>
<td>1.61</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>32.1</td>
<td>57.6</td>
<td>45.9</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>27.3</td>
<td>54.7</td>
<td>43.6</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>37.4</td>
<td>47.9</td>
<td>42.9</td>
<td>3.89</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>36.0</td>
<td>50.1</td>
<td>44.9</td>
<td>2.46</td>
</tr>
<tr>
<td>V20</td>
<td>10</td>
<td>33.6</td>
<td>51.3</td>
<td>45.9</td>
<td>1.72</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>30.6</td>
<td>51.8</td>
<td>46.4</td>
<td>1.07</td>
</tr>
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<td></td>
<td>40</td>
<td>25.4</td>
<td>46.8</td>
<td>41.9</td>
<td>0.35</td>
</tr>
</tbody>
</table>

a) Per gram of total samples
b) Based on unit mass of PCL component, and 139.5 J/g heat of fusion of 100% crystalline PCL
From the DSC data, we calculate the relative degree of crystallinity $X(T)$ at different crystallization temperatures $T_c$, as shown in Figure 9. The crystallinity is calculated from the expression:

$$X(T) = \frac{\int_0^T \left( T \right) dT}{\int_0^{T_c} \left( T \right) dT}$$

During the nonisothermal crystallization, we obtained a series of reversed S-shaped curves. A relationship between $T_c$ and crystallization time $t$ is given as follows:

$$t = \frac{|T_0 - T_c|}{R}$$

where $T_0$ is the initial temperature when crystallization begins and $R$ is the cooling rate. With equation (2), the temperature axis in Figure 9 can be transformed into a timescale in Figure 10.

The nonisothermal crystallization kinetics analysis is of practical importance since it can reflect the crystallization behaviour of polymers under processing conditions. Several theoretical methods have been employed to predict and analyze kinetics of nonisothermal crystallization, and one of the most commonly used was proposed by Ozawa analysis in nonisothermal crystallization kinetics.
Ozawa. Considering the effect of the cooling rate $R$ on the crystallization kinetics, Ozawa [32] extended the Avrami equation to nonisothermal crystallization, as follows:

$$1 - X(T) = \exp\left[-\frac{K(T)}{R^m}\right]$$

$$\log\left\{\ln[1 - X(T)]\right\} = -m \log R + \log K(T)$$

where $X(T)$ is the relative degree of crystallinity, $m$ is the Ozawa exponent, and $K(T)$ is the kinetic crystallization rate constant. A plot of $\log \{\ln [1 - X(T)]\}$ vs. $\log R$ at a given temperature should result in a straight line if the Ozawa method is valid. We get a straight line for PCL in Figure 11; however we do not obtain straight lines for PCL/PVP blends in the figure. This experimental fact indicates that the Ozawa equation is not suitable to describe the kinetics in the nonisothermal crystallization of PCL/PVP blends, which has an appreciable extent of secondary crystallization.

**Fig. 11.** Plots of $\log\{\ln[1 - X(T)]\}$ vs. $\log R$ from the Ozawa equation for PCL, and V10, V20 blends.

**Combined Avrami and Ozawa equations**

To find a method to describe properly the nonisothermal crystallization process, Liu and coworkers [33] proposed a novel method for nonisothermal crystallization process and successfully dealt with the nonisothermal crystallization behaviour of nylon-11 [34], PEDEKK [35], nylon-66 [36], nylon-46 [37], nylon-1212 [38], syndiotactic polystyrene [39], PP–PP-g-MAH–Org–MMT [40], and PETIS [41]. They obtained the following equation:

$$\log R = \frac{1}{m} \log\left(\frac{K(T)}{Z_r}\right) - \frac{n}{m} \log t$$

Defining $F(T) = [K(T)/Z_r]^{1/m}$ and $\alpha = n/m$, the parameter $F(T)$ is a measure of the cooling rate which has to be chosen at the unit crystallization time to achieve a certain degree of crystallinity. The smaller the value of $F(T)$, the higher the crystallization rate becomes. With the above assumption, Liu and coworkers obtained the following expression (Mo–Liu equation):

$$\log R = \log F(T) - \alpha \log t$$

According to Equation (6), the plots of $\log R$ vs. $\log t$ at a given relative degree of crystallinity are shown in Figure 12. Using straight lines to fit these data, we obtain a series of lines with the slope = $-\alpha$ and intercept=$\log F(T)$. The values of $\alpha$ and $F(T)$ are...
listed in Table 3. It is apparent that the F(T) values increase systematically with increasing relative degree of crystallinity, indicating that at a unit crystallization time, higher cooling rate should be used to obtain a higher degree of crystallinity; however, the values of α are approximately constant.

**Tab. 3.** α and F(T) at the relative crystallinites X(t) of PCL and PCL/PVP blends.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Variable</th>
<th>X(t)(%)</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL</td>
<td>α</td>
<td></td>
<td>1.01</td>
<td>1.04</td>
<td>1.05</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td>F(T)</td>
<td></td>
<td>5.62</td>
<td>6.76</td>
<td>7.59</td>
<td>9.55</td>
</tr>
<tr>
<td>V10</td>
<td>α</td>
<td></td>
<td>1.66</td>
<td>1.61</td>
<td>1.62</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>F(T)</td>
<td></td>
<td>18.20</td>
<td>20.42</td>
<td>22.39</td>
<td>25.71</td>
</tr>
<tr>
<td>V20</td>
<td>α</td>
<td></td>
<td>6.35</td>
<td>6.53</td>
<td>6.40</td>
<td>6.97</td>
</tr>
<tr>
<td></td>
<td>F(T)</td>
<td></td>
<td>3.8×10^{10}</td>
<td>6.8×10^{10}</td>
<td>8.7×10^{10}</td>
<td>6.6×10^{11}</td>
</tr>
</tbody>
</table>

**Fig. 12.** logR vs. logt from the combined Avrami and Ozawa equation for PCL and PCL/PVP blends.

**Fig. 13.** Dependency of the melt-crystallization peak temperature T_c on the cooling rate R for PCL and PCL/PVP blends.

**Crystallization rate coefficient**

To allow a direct comparison of the crystallization rates of various polymers on a single scale, empirical methods were proposed [42-44]. Among them, Khanna [42] introduced a “crystallization rate coefficient” (CRC) which can be measured from the slope of the plot of cooling rate versus crystallization peak temperature and used as
a guide for ranking the polymers on a scale of crystallization rates. The CRC values are higher for faster crystallization systems. According to Khanna’s treatment, the cooling rate R is plotted against Tc, as shown in Figure 13. The CRC value for PCL obtained from the slope of the line is 3.86 min\(^{-1}\). Compared with the values calculated for PCL/PVP blends, it is appreciably higher (3.24 and 3.12 min\(^{-1}\) for V10 and V20, respectively). Consequently, PVP has a restrain effect on the crystallizability of PCL, and the crystallization rate of PCL/PVP blends decreases when the PVP content in the blends increases.

**Conclusions**

We studied thermomechanical behaviour and nonisothermal crystallization of PCL and the PCL/PVP blends using DMA and DSC methods. The DMA results show that the Tg is higher for PCL/PVP blends than for pure PCL, and the apparent activation energy at Tg being higher for PCL/PVP blends. The temperature dependence of E’ shows that PVP has a reinforcement effect in PCL. At 37 °C, both materials exhibit interesting damping properties (especially PCL/PVP blends) which may be relevant in orthopedic applications, as it may help in the dissipation of the mechanical energy generated by the patient movements. Two different analytical methods are explored to investigate the nonisothermal crystallization behaviour of the samples. The Ozawa equation fails to describe the nonisothermal crystallization kinetics for the PCL/PVP blends, whereas the Mo–Liu equation successfully describes kinetics of the nonisothermal process for PCL and PCL/PVP blends. Based on Khanna’s method, the CRC value calculated for PCL is compared with the values obtained for PCL/PVP blends. The results show that PCL has a high crystallization rate relative to PCL/PVP blends, and that PVP has a restrain effect for PCL crystallization in blends.

**Experimental part**

**Materials and preparation**

\(\varepsilon\)-Caprolactone, CL (Aldrich, Shanghai, China) was dried over CaH\(_2\) for 1 week and distilled at reduced pressure prior to use. N-Vinylpyrrolidone, NVP (Shanghai povidone trade Company, Shanghai, China) was dried under reduced pressure for several hours to remove trace of water before use. Azodisobutyronitrile (AIBN), ethyleneglycol and Tin(II) octanoate (Sn(Oct)\(_2\)) used in this study were all purchased from Shanghai Chemical Reagents Company(Shanghai, China) and used without further treatment. The synthesis procedures are shown in Figure 1. The PCL/PVP blends obtained were denoted as V10 blend (PVP 10 wt %), V20 blend (PVP 20 wt %). The Waters 991 GPC model was used to evaluate the average molecular weight (M\(_w\)) of PCL and PVP and the polydispersity (M\(_w\)/M\(_n\)) of blends. The molecular weights were calibrated with polystyrene standards. The M\(_w\) of the PCL was over 6.0×10\(^4\) g mol\(^{-1}\), and the polydispersity (M\(_w\)/M\(_n\)) of it was 1.38~1.5. The M\(_w\) of the PVP was 1.2×10\(^4\) g mol\(^{-1}\), and the polydispersity of it was 1.4~1.6.

**Dynamic Mechanical Analysis**

Dynamic mechanical analysis (DMA) testing was carried out using Mettler DMA861 equipment. The samples were obtained by compression molding at a constant force of 10 tons at 65 °C for 20 min and then cut into bars of about 40×13×1 mm\(^3\). The testing configuration was three-point bending. A constant dynamic force of 5×10\(^5\) Pa was applied and five different frequencies were used (1, 5, 10, 50,100 Hz). The
characterization of the glass transition was carried out by the tests performed in the temperature range of -140 to 50 °C at a heating rate of 5 °C·min⁻¹.

**Differential scanning calorimetry**

Isothermal and nonisothermal crystallization kinetics were studied using a Perkin–Elmer DSC-7 differential scanning calorimeter (Perkin Elmer Cletus Instruments, Norwalk, CT), where the temperature was calibrated with an indium standard. All DSC measurements were performed under a nitrogen atmosphere, and sample weights varied from 6 to 8 mg. After erasing the previous thermal history, nonisothermal crystallization kinetics was performed by the cooling of the melts at five different cooling rates (2.5, 5, 10, 20, 40 °C/min, respectively). The exothermic curves of heat flow, as a function of temperature, were recorded and investigated.

**References**