Effect of nucleation and plasticization on the crystallization of poly(lactic acid)

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Abstract

In this paper, different strategies to promote PLA crystallization were investigated with the objective of increasing the crystalline content under typical polymer processing conditions. The effect of heterogeneous nucleation was assessed by adding talc, sodium stearate and calcium lactate as potential nucleating agents. The PLA chain mobility was increased by adding up to 10 wt% acetyl triethyl citrate and polyethylene glycol as plasticizers. The crystallization kinetics were studied using DSC analysis under both isothermal and non-isothermal conditions. The isothermal data showed that talc is highly effective in nucleating the PLA in the 80–120 °C temperature range. In the non-isothermal DSC experiments, the crystallinity developed upon cooling was systematically studied at cooling rates of 10, 20, 40, and 80 °C/min. The non-isothermal data showed that the combination of nucleant and plasticizer is necessary to develop significant crystallinity at high cooling rates. The nucleated and/or plasticized PLA samples were injection molded and the effect of mold temperature on crystallinity was determined. It was possible to mold the PLA formulations using mold temperatures either below 40 °C or greater than 60 °C. At low temperature, the molded parts were nearly amorphous while at high mold temperatures, the PLA formulation with proper nucleation and plasticization was shown to achieve crystallinity levels up to 40%, close to the maximum crystalline content of the material. Tensile mechanical properties and temperature resistance of these amorphous and semi-crystalline materials were examined.
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1. Introduction

Poly(lactic acid) (PLA) is a commercially available bio-based material that could become a material of choice, especially in packaging applications due to its good clarity, high strength and moderate barrier properties. The expected rise in the cost of petroleum-based commodities in the next decades opens a bright perspective for this material. Its compostability can also be an asset in applications that are difficult to recycle. It is in many ways similar to poly(ethylene terephthalate) (PET). It is a highly transparent and rigid material with a relatively low crystallization rate that makes it a promising candidate for the fabrication of biaxially oriented films,

thermoformed containers and stretch-blown bottles [1,2]. Recently, more attention has been turned to the study of PLA crystallization kinetics. In many applications, increasing the crystallization speed of PLA is desired since in its amorphous form, the range of application of PLA is severely limited by its low glass transition temperature [3]. At temperatures greater than PLA's T_g, around 56 °C, only the crystalline PLA phase can confer useful mechanical properties. Thus, the crystalline form is required to increase the temperature resistance of the material. At its maximum, the PLA crystalline content reaches around 40%. We will refer to this as the fully crystallized state implying that the crystallinity level has reached its maximum value. It has also been reported that the tensile and flexural moduli of fully crystallized poly(L-lactic acid) (PLLA) are approximately 10% higher than that of amorphous PLA [4].

Commercially available PLA grades are obtained by ring-opening polymerization of lactide, a dimer of lactic acid.

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Lactic acid is optically active and thus can be of L or D form. The maximum attainable crystallinity level is obtained by minimizing the amount of D-lactide isomers and of L,D-lactide (i.e. mesolactide) in the L-lactide used as the major monomer. The crystallinity and crystallization rate obviously decrease as the purity in crystallizable L-LA segment decreases. For example, the crystallization half-time was found to increase by roughly 40% for every 1 wt% increase in the mesolactide content of the polymerization mixture [5]. Even at high L-LA content, however, PLA crystallization is typically too slow to develop significant crystallinity unless the crystallization is induced by strain such as in processes used to produce biaxially oriented films or bottles. In processes such as injection molding, where the orientation is limited and the cooling rate is high, it is much more challenging to develop significant crystallinity and thus formulation or process changes are required. Three routes may be considered. The first one is to add a nucleating agent that will lower the surface free energy barrier towards nucleation and thus initiates crystallization at higher temperature upon cooling. A second possibility is to add a plasticizer which will increase the polymer chain mobility and will enhance the crystallization rate by reducing the energy required during crystallization for the chain folding process. Finally, a third possibility is to play with the molding conditions, in particular molding temperature and duration.

Several potential nucleating agents have been examined in the literature. One for which there were high hopes is the stereocomplex of PLLA and PLDA. It has been reported that mixing of PDLA and PLLA in solution can lead to the formation of a stereocomplex between the two different helical polymer chains [6]. At a 50/50 blend ratio, the stereocomplex has a melting temperature of 230 °C, which is 50 °C higher than that of the pure PLLA or PDLA. It was also reported that the overall crystallization rate of 1:1 PLLA/PDLA stereocomplexes was higher than that of pure PLLA or PDLA, due to higher radius growth rate and density (number per unit area or volume) of the stereocomplex spherulites and a shorter induction period for the formation of spherulites [7]. Stereocomplexation was found to be preferred over homopolymer crystallization even when the D-content in the PDLA phase was lowered to 80%. In that case, the crystallization rate of the stereocomplex was reduced to the same range as that of the homopolymers. This match in crystallization rate provided favorable conditions for epitaxial growth of the homopolymer crystals unto the stereocomplex. No homopolymer nucleation was found, however, in the case of the symmetric PLLA/PDLA complex [8]. Yamane and Sasai [9] investigated the thermal property and non-isothermal crystallization behavior of PLLA blended with a small amount of PDLA (1—5 wt%). Low molecular weight PDLA isolated in the matrix of PLLA did not form a stereocomplex crystallite with a surface area large enough to act as a nucleation site. On the other hand, high molecular weight PDLA chains formed a large stereocomplex crystallite. With increasing PDLA content, stereocomplex crystallites were more easily formed and acted as nucleation sites, which effectively increased the number of PLLA spherulites, and therefore, the overall crystallization

rate. This effect disappeared, however, when the blend was completely molten (past the 240 °C melting temperature of the strereocomplex) prior to cooling, which seemed to indicate that the crystallization of the stereocomplex was not fast enough to form the crystalline structures required to nucleate the bulk of the material. More recently, Tsuji et al. [10] studied the isothermal and non-isothermal crystallization behavior of blends of PLLA with 0.1—10 wt% PDLA. The addition of PDLA was shown to increase the number of spherulites in isothermal experiments but did not modify the crystal growth rate or the mechanical properties of crystallized films. Overall, the crystallization half-time was reduced only when 10% of PDLA was used and the reduction was around 50% in the optimal crystallization temperature range. Smaller PDLA concentration resulted in no change or increased crystallization half-time.

Another class of potential nucleating agents is sodium salts. In PET, another polyester suffering from slow crystallization kinetics, sodium benzoate and its derived salts were shown to be effective nucleating agents. The mechanism proceeds through decomposition of the salt and reaction of the sodium ions with the acid end-groups of the polyester, resulting in polymeric ionomers that then form clusters and act as nucleating species [11,12]. The use of sodium salt in PLA as a nucleating agent has not yet been explored.

Talc is another widely used nucleating agent. It was shown that talc nucleates the crystallization of polymers through an epitaxial mechanism [13]. In the case of PLA, it is shown that the crystallization half-time can be reduced by more than one order of magnitude to less than 1 min when 1% talc is added [14]. Similarly, strong increase in nucleation density with addition of talc was found in poly(L-lactide-*co*-mesolactide) [5].

The use of organically treated montmorillonite (MMT) clay has been investigated as a mean to increase crystallinity and to improve the thermal and mechanical properties of PLA [15]. In one study using a PLA containing 4% D-LA, it was found that the clay reduced slightly the crystallization rate upon heating and shifted cold crystallization temperature to higher values when compared with the neat PLA, possibly due to reduced chain mobility [16]. In another systematic crystallization study on a PLA comprising 1.1—1.7% D-LA, it was found that the nucleation rate of PLA was slightly increased after addition of an organically treated C18-MMT while the linear growth rate of PLA spherulites remained unchanged [17]. An overall crystallization rate increase of 30% was observed. This rate increase is relatively modest when compared to that observed with talc. Therefore, clays are less effective than talc as nucleating agents for PLA.

Recently, research efforts have shown that organic compounds can nucleate the crystallization of PLA. In one study, an aliphatic amide (AA), namely *N,N*-ethylenebis(12-hydroxystearamide) was used. This compound has a melting temperature similar to that of PLA but is able to crystallize faster upon cooling. The organic AA crystallites act as nucleating agents for PLA crystallization, resulting in 10-fold increase in nucleation density and in 5-fold increase in overall

crystallization rate [18]. In another study, a series of organic compounds having hydrazide end-groups were evaluated in terms of their nucleating abilities. Best results, obtained with benzoylhydrazide compounds, showed increased crystallization temperature upon cooling and led to fully crystallized samples at moderate cooling rates (−20 °C/min) [19]. Unfortunately, these compounds are not readily available as they have only been synthesized at the laboratory scale.

Another chemical compound that has been reported to be effective in nucleating crystallization in PLA is calcium lactate. It was reported that addition of 1% calcium lactate increased the crystallization rate of a 90:10 L/D,L-PLA copolymer to the point where samples were completely crystallized from the melt within the process time of an injection molding cycle [3]. This information which can have a great impact considering the relative low cost and availability of this chemical has not, however, been corroborated by any subsequent studies.

The second route towards increased crystallization rate is the addition of a plasticizer to increase chain mobility and extend the crystallization temperature window. Previous studies focused on blending PLA with various low molecular weight plasticizers such as citrate esters, triacetine, poly(ethylene glycol), poly(propylene glycol), and glycerol were aimed at modifying its inherent brittle behavior [20–29]. The presence of a plasticizer decreases the glass transition temperature of PLA, reducing the aging effects typically found in neat PLA and improving its ductility and drawability thus broadening the range of potential applications [21]. Poly(ethylene glycol) (PEG) is the most studied plasticizer for PLA, and the efficiency of plasticization is increased with decreasing molecular weight. The T_g was shown to be depressed from 58 °C for pure PLA to 41 and 30 °C, respectively, at 10 and 20% PEG loading levels for PEG molecular weight of 1500 [20]. The T_g can be further depressed using a lower PEG molecular weight of 400, to 30 and 12 °C, respectively, and the elongations at break were 26 and 160%, respectively, at those same PEG loading levels. In another study, it was also shown that low molecular weight PEG could accelerate the spherulite growth rate [21]. When using high PEG concentration (e.g. 30 wt%), it was shown that blends of PLA and PEG could undergo phase separation and that the blends were not stable at ambient temperature due to epitaxial crystallization of PEG on the edge of the PLA spherulites [29].

Most crystallization studies are carried out in quiescent conditions using thermal analysis techniques. The crystalline levels achieved in molded or extruded articles can be strongly influenced by the flow and orientation prevailing while the polymer is being cooled and crystallized. There is currently no systematic study on the effect of molding conditions on the crystalline development in PLA. Recently, however, it was shown that PLA nucleated with organic compounds (benzoylhydrazide compounds) could be molded into highly crystalline parts [30]. The increased heat distortion temperature, over 120 °C, clearly exhibits the benefits of fully crystallized PLA. Even though the reported crystallization half-time in the 90–130 °C temperature range was below 45 s, the

necessary molding cycle time to achieve undistorted parts was in excess of 3 min at a mold temperature of 110 °C. It is clear that the cycle time and mold temperature must be decreased dramatically in order to render the molding process economically viable.

In this paper, we investigate the effect of nucleation and plasticization on the crystalline content developed in quiescent isothermal and non-isothermal conditions and in injection molding conditions. Surprisingly, there is very little literature examining the combined effects of nucleation and plasticization on the crystallization kinetics. Combining nucleating agents and plasticizers could have a synergistic effect on PLA crystallization kinetics, due to the improved chain mobility and the enhanced nucleating ability. The nucleating ability of talc, sodium stearate and calcium lactate was assessed while ATC and PEG were used as plasticizers. The crystalline content and properties achieved in different conditions are compared using DSC, tensile mechanical testing and dynamic mechanical analysis.

2. Experimental

2.1. Materials

The poly(lactic acid) supplied by NatureWorks was a semi-crystalline grade (PLA 4032D) comprising around 2% D-LA. Talc, sodium stearate and calcium lactate were evaluated as potential nucleating agents. The talc was Mistron Vapor R supplied by Luzenac America. The sodium stearate (Na-St) was supplied by Blachford Co. Calcium lactate was obtained from Aldrich chemicals. Polyethylene glycol (PEG) and acetyl triethyl citrate (ATC) were used as PLA plasticizers. The PEG had a molecular weight of 3350 g/mol and a melting point of 56 °C. It was manufactured by Dow Chemicals under tradename Carbowax 3350. The ATC was supplied by Morflex Inc. under tradename Citroflex-4.

2.2. Sample preparation

Mixtures of PLA with various contents of plasticizers and nucleating agents were prepared on a Leistritz 34 mm co-rotating twin-screw extruder. The PLA was dried at 65 °C for 8 h in a desiccant dryer prior to extrusion while the plasticizers and nucleating agents were used as received. Since it was difficult to precisely dose the plasticizers and nucleants at concentrations below 5%, it was decided to first prepare 20% concentrates and then to dilute these concentrates to the desired final concentration in a second step. Each extrusion step was carried out at a relatively low extrusion temperature of 180 °C and using a high flow rate to minimize the residence time and thus the degradation during processing. The mixtures were extruded using a 2-strand die, water cooled and pelletized in preparation for the injection molding process. The samples were dried again at 40–60 °C, depending on the plasticizer level for 24 h prior to injection molding and to subsequent DSC analysis.

2.3. Rheological characterization

The rheological properties of PLA with various plasticizer contents of PEG and ATC, with 1% talc and 0.5% Na-St were measured at 180 °C using a rotational rheometer with a plate–plate geometry in dynamic mode. The complex viscosity was monitored over time to verify the thermal stability of the samples. Frequency sweeps were carried out to determine the complex viscosity over a frequency range of 0.1–100 rad/s. Care was taken to dry the samples prior to testing and to keep them under a nitrogen blanket during testing to minimize oxidation and to maintain a dry environment.

2.4. Differential scanning calorimetry (DSC)

Isothermal crystallization was performed using a differential scanning calorimeter (DSC) Perkin–Elmer DSC 7 system in the temperature range of 80–120 °C. The DSC was calibrated using the melting temperature and enthalpy of indium. The samples with a weight around 10 mg were put into an aluminum pan and hermetically sealed. The sample was first completely melted and relaxed by heating it from 20 to 200 °C at 20 °C/min and maintaining it at 200 °C for 2 min. Subsequently, it was rapidly cooled (−100 °C/min) to the isothermal crystallization temperature and held there until completion of crystallization. Once crystallized, the samples were reheated to 200 °C at a rate of 20 °C/min in order to measure the melting endotherm.

For the non-isothermal crystallization, the samples were heated to 200 °C and kept in the molten state for 2 min to erase the prior thermal history. The samples were then cooled at cooling rates of 10, 20, 40 or 80 °C/min down to 20 °C to evaluate their ability to crystallize upon cooling. Subsequently, the samples were heated back to 200 °C at a rate of 20 °C/min to assess the crystallization upon heating (if any) and to verify that the melting enthalpy corresponds to the sum of the cooling and heating crystallization enthalpies. The crystallization exotherms and peak crystallization temperature were measured.

2.5. Mechanical characterization

The tensile testing was carried out at a rate of 5 mm/min according to ASTM D638 on standard type I dog-bone shaped samples with sample thickness of 3.1 mm. The samples were injection molded and were conditioned at room temperature for a period of 4 weeks prior to testing. This period allowed aging of the PLA and enabled to obtain measurement that were constant with time.

2.6. Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical properties of the materials were measured in bending mode in a DMTA Mk III from Rheometric Scientific Ltd. The 14 × 32 mm rectangular samples were cut out from the injection molded samples and machined to a thickness of 1.45 mm. The probing frequency was 1 Hz and the samples were heated at the rate of 2 °C/min.

3. Results and discussion

3.1. Rheology

The melt viscosity of polymers is very sensitive to changes in the macromolecular chain structure and to the addition of plasticizers which by definition increases the polymer free-volume and the polymer chains' mobility. Therefore, the rheology is of practical and fundamental interest in the current study. Fig. 1 presents the viscosity of PLA and of various PLA formulations at 180 °C as a function of oscillation frequency. In the embedded graph, the viscosity for a fixed oscillation frequency of 1 rad/s is presented as a function of time. The viscosity of PLA and PLA with 10% ATC or 10% PEG is relatively stable over a period of 1800 s (30 min) which means that no obvious degradation or phase separation occurred. The pure PLA exhibits a clear Newtonian Plateau at low oscillation frequency with a zero-shear viscosity around 5 kPa s. The measurement for pure PLA was obtained from oscillatory measurement carried out on virgin pellets, while for all formulations, it was carried out on the twin-screw extruded pellets. In prior work, however, with a similar compounding process, it was shown that the PLA rheology was nearly unaffected by a first extrusion pass [31]. Further evidence for this comes from the viscosity of the compounded formulation comprising 1 wt% talc. At this level (corresponding to less than 0.5% on a volume basis), the presence of talc is not expected to change the viscosity and therefore the observed small viscosity drop upon compounding confirms the PLA stability during the extrusion step. The situation is quite different when we add only 0.5% sodium stearate (Na-St) to PLA. In this case, the plateau viscosity drops to 2 kPa s, a 2.5-fold decrease when
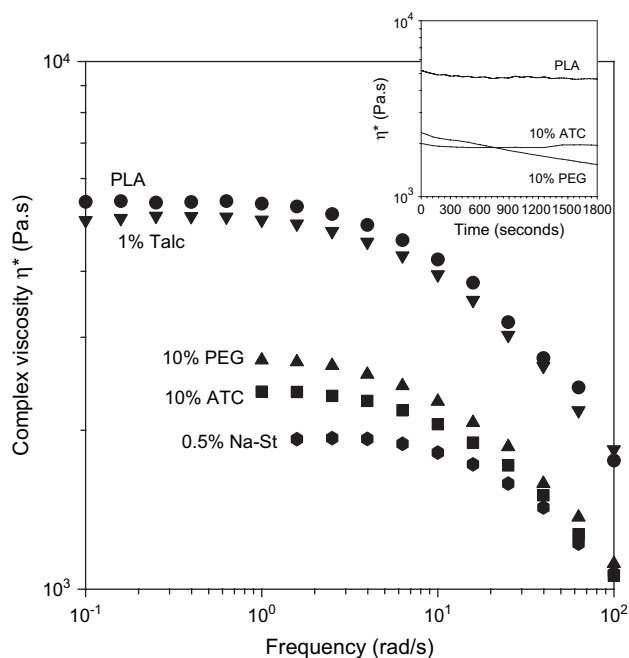

Fig. 1. Complex viscosity for selected PLA formulations. Embedded figure: time sweep for PLA and plasticized PLA formulations.

compared to the pure PLA control. It has been reported that the presence of so-called ''chemical'' nucleating agents such as calcium stearate will induce polymer chain scission and then react with acid end-groups leading to the formation of a polyester ionomer [11]. We will examine later the nucleating potential of calcium stearate but it is clear that any nucleating effect comes at a relatively high cost in terms of chain scission. Fig. 1 also presents the viscosity of the PLA plasticized using 10% ATC and 10% PEG, respectively. Both ATC and PEG are good plasticizers for PLA and effectively decrease its viscosity. The effect of the plasticizer content is further explored in Fig. 2 where the zero-shear viscosity is presented as a function of the plasticizer content. The viscosity follows an exponential decay with plasticizer content which is a typical plasticizer content effect. At high plasticizer content, a leveling off of the viscosity is expected if the plasticizer saturation point is reached resulting in phase separation. This effect is not observed in the investigated concentration range confirming that we are well within the plasticizer solubility limit in PLA. Based on the figure, the ATC is slightly more effective in reducing PLA viscosity than the PEG. This statement may be specific to the molecular weight of the PEG used here. Lower molecular weight chemicals will tend to be more efficient plasticizers if used on the same weight basis.

3.2. Non-isothermal crystallization kinetics

The effect of plasticization and nucleation on PLA's non-isothermal crystallization kinetics was investigated. The DSC thermograms obtained for the cooling rate of 20 °C/min with various compositions are shown in Fig. 3. As expected, the neat PLA exhibited no crystallization peak upon
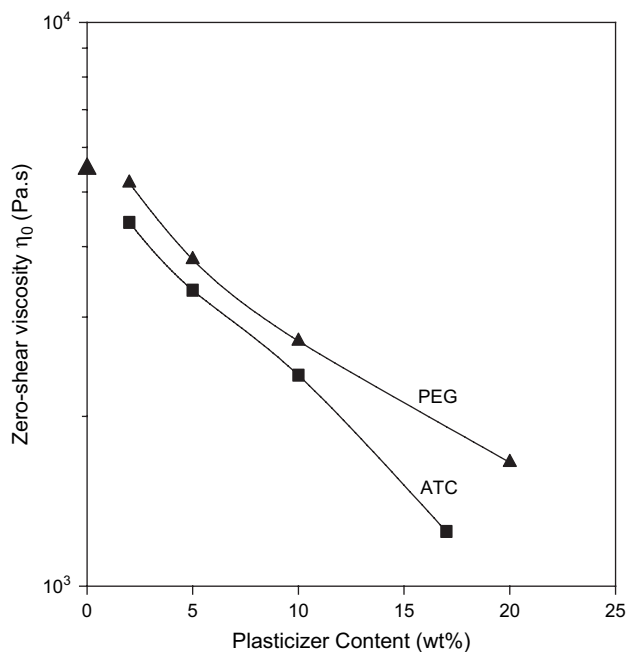
cooling and no significant crystallization endotherm upon heating. At 5% PEG plasticizer concentration, there is still no discernible crystallization peak upon cooling. However, a crystallization peak upon heating appeared at around 110 °C showing that the increased chain mobility already increased slightly the ability of PLA chains to crystallize. As the PEG content was increased up to 10%, a weak and broad crystallization peak upon cooling appears with a peak temperature around 80 °C. The higher plasticizer concentration shifted the crystallization peak upon heating to a lower temperature, around 90 °C. This can be associated to two different phenomena. The first one is the increased chain mobility at low temperature associated with the larger T_g depression. This T_g reduction enables crystallization to start at an earlier temperature upon heating. A second phenomenon is the reduced crystallization induction period due to the presence of crystalline nuclei already formed during the cooling process. Even though these nuclei may represent a small crystalline fraction in absolute term, they will increase the crystallization rate upon heating since the crystalline structure is already more densely nucleated than when the polymer is being cooled from the melt. Thus the combination of reduced T_g and higher nucleation density resulted in crystallization peaks that shifted to a lower temperature as the plasticizer content was increased.

The addition of calcium lactate, sodium stearate and talc can also be compared as given in Fig. 3. The first two had very limited effect on the PLA thermograms. In the case of

Fig. 2. Effect of plasticizer content on the zero-shear viscosity of PLA at 180 °C.
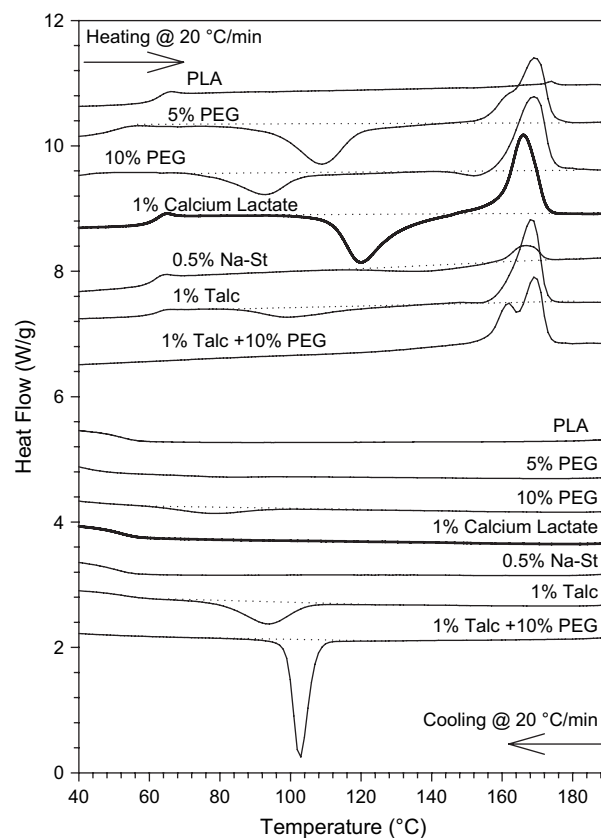

Fig. 3. DSC thermograms for PLA and PLA formulations cooled at 20 °C/min and subsequently heated at 20 °C/min.

sodium stearate, a very weak and broad crystallization endotherm was found around 130 °C and was supported by the subsequent weak melting peak. In the case of calcium lactate, there is no discernible crystallization peak upon cooling and a broad cold crystallization peak appears around 95 °C upon heating. The effect of talc, however, was more pronounced. At 1% talc loading, a much sharper crystallization peak was observed upon cooling. The peak occurred at 90 °C which is higher than that at the 10% plasticizer level. Talc by itself, however, did not enable the development of a high crystalline content upon cooling at 20 °C/min. Similarly, upon reheating, the crystallization peak was relatively weak and as expected from chain mobility arguments the peak temperature occurred at higher temperature than that in the plasticized materials. The most dramatic effects on the crystallization kinetics were observed when talc and the plasticizer were added simultaneously. At 1% talc and 10% PEG concentrations, a very sharp crystallization peak upon cooling was found and this peak was shifted up to 105 °C. On subsequent heating, no crystallization peak was observed since the PLA was already crystallized to its maximum in the cooling cycle. Thus the simultaneous use of a plasticizer and an effective nucleating agent had a synergistic effect which significantly expanded the crystallization window by increasing the nucleation rate in the upper temperature window and increasing the chain mobility in the lower temperature range. It is noteworthy that similar measurements were carried out with the ATC plasticizer and that qualitatively the same phenomena were observed. These results are not shown here for the sake of conciseness but will be discussed while quantifying the peak temperature and heat of crystallization.

In order to quantify the effects of the plasticization and nucleation, the peak crystallization temperature upon cooling T_{cc} and the crystallization enthalpy upon cooling ΔH_{cc} were measured for plasticizer concentrations of 2, 5, 10% and cooling rates at 10, 20, 40, 80 °C/min. To make sure the crystallization endotherms were correctly integrated, it was systematically verified in the subsequently heating run that the melting enthalpy ΔH_m was equal to the sum of the measured crystallization enthalpy upon cooling (ΔH_{cc}) and heating (ΔH_{ch}). The effect of talc concentration on the peak crystallization temperature upon cooling, T_{cc}, and on the crystallization enthalpy upon cooling ΔH_{cc} is presented in Fig. 4. As noted above, there were no crystallization endotherms when no talc was added. The first reported data points are thus for a talc content of 1%. At that level, as shown in Fig. 4a, a T_{cc} value of 104 °C was found with a cooling rate of 10 °C/min and that value decreased as the cooling rate was increased. At all cooling rates, the T_{cc} was increased by 2–3 °C when the talc concentration was increased from 1 to 2% and then increased linearly by 0.5 °C/% talc. Therefore as expected the use of a greater talc concentration initiates faster crystallization thus widening the crystallization temperature window of the material. It is important to see how this affects the final crystallinity developed upon cooling. The developed crystallinity is presented in terms of ΔH_{cc} in Fig. 4b. At a cooling rate of 10 °C/min, the developed crystallinity ΔH_{cc} was independent of the talc
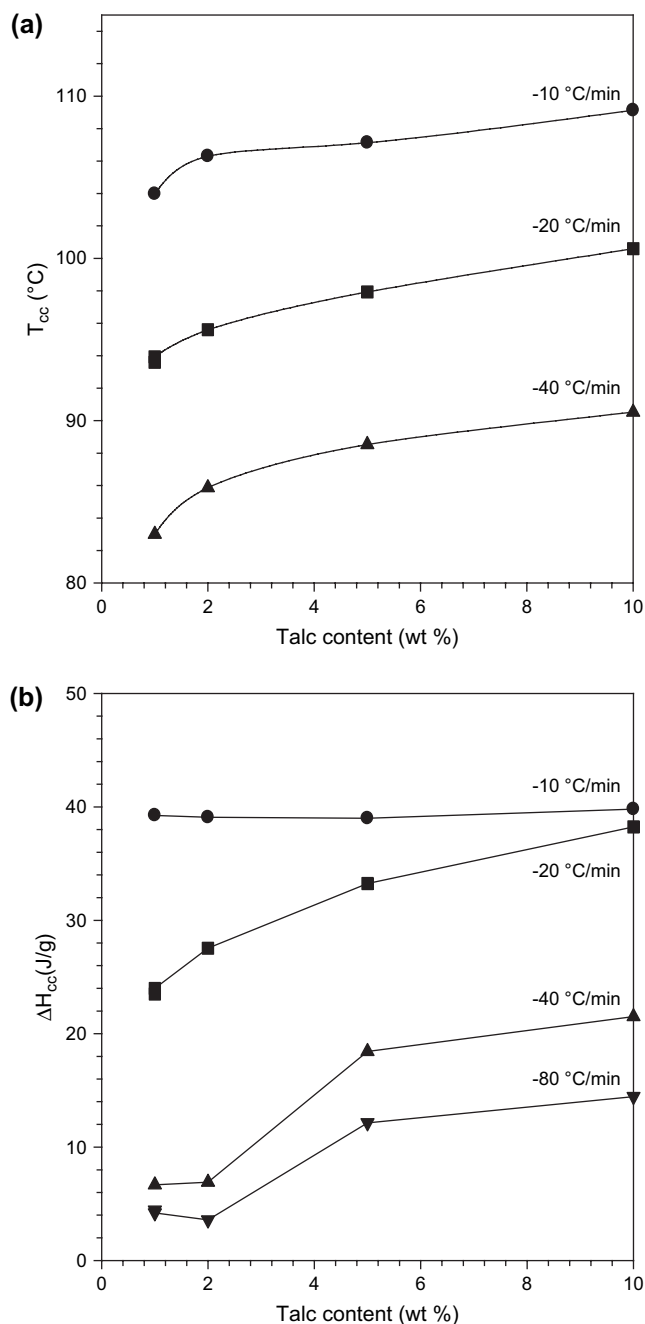

Fig. 4. Effect of talc content on (a) peak crystallization temperature upon cooling T_{cc} and (b) crystallization enthalpy upon cooling ΔH_{cc}.

content and remained around 40 J/g. PLA is expected to crystallize up to a maximum level of 40–45% which corresponds to 37–42 J/g endothermal peaks (using 93 J/g as the theoretical value for the heat of fusion of PLA crystals [32]). Thus, the measured ΔH_{cc} clearly correspond to the maximum crystalline level for PLA grade under study. As the cooling rate was increased, the crystallinity achieved decreased and this effect was accentuated at the lower talc concentration. At a cooling rate of 80 °C/min, only samples containing 5 and 10% talc exhibited significant crystallinity. The cooling rate in injection molding operation can be much higher than 80 °C/min and it can therefore be anticipated that the use of talc alone in

a PLA formulation is not sufficient to achieve highly crystallized parts.

Fig. 5 shows similar data as Fig. 4, but in this case the ATC and PEG contents rather than the talc content are varied. All data are for 1% talc loading level. Data obtained without talc cannot be represented since no significant crystallization peaks are observed. The peak crystallization temperature T_{cc} presented in Fig. 5a was nearly independent of plasticizer level in the 0–5% range. A priori the use of the plasticizer should not affect the T_{cc} since the crystallization upon cooling is initiated in the upper crystallization temperature window where

(a)

(b)

Fig. 5. Effects of plasticizer content on (a) peak crystallization temperature upon cooling T_{cc} and (b) crystallization enthalpy upon cooling ΔH_{cc}.

crystallization is limited by the nucleation rate rather than by the chain mobility. However, at 10% plasticizer level, significant changes in T_{cc} are measured. In the case of PEG, the crystallization peak was significantly sharpened as the plasticizer level was increased and this pushed up the peak crystallization temperature T_{cc} closer to the onset crystallization temperature. With the addition of ATC, as we will discuss below, complete crystallization is not achieved at high cooling rates. The increase in plasticizer level enabled the crystallization to proceed in a lower temperature range and thus pushed the T_{cc} downward. The most important finding concerning the use of the plasticizer can be found in its effect on the achieved crystallinity upon cooling at high cooling rates, as shown in Fig. 5b. At the 10% PEG level, the PLA reached nearly its maximum crystallinity even at the 80 °C/min cooling rate. Even at 5% PEG loading, the ΔH_{cc} reached a high value of 37 J/g at 40 °C/min cooling rate and a significant ΔH_{cc} of 18 J/g was attained at 80 °C/min. Nearly no effect on crystallization was found when the PEG was used at 2% loading. ATC has also a positive effect on the crystallinity achieved upon cooling when used at 5% loading and up. At 10% ATC level, the PLA nearly reaches its maximum crystallinity level with $\Delta H_{cc} = 37$ J/g at 40 °C/min cooling rate while much lower crystallinity is achieved at 80 °C/min compared to PEG. Thus ATC is slightly less effective than PEG in promoting crystallinity at high cooling rates. It is noteworthy that at that same cooling rate of 80 °C/min, the PLA with 1% talc and no plasticizer developed very little crystallinity with $\Delta H_{cc} = 6$ J/g.
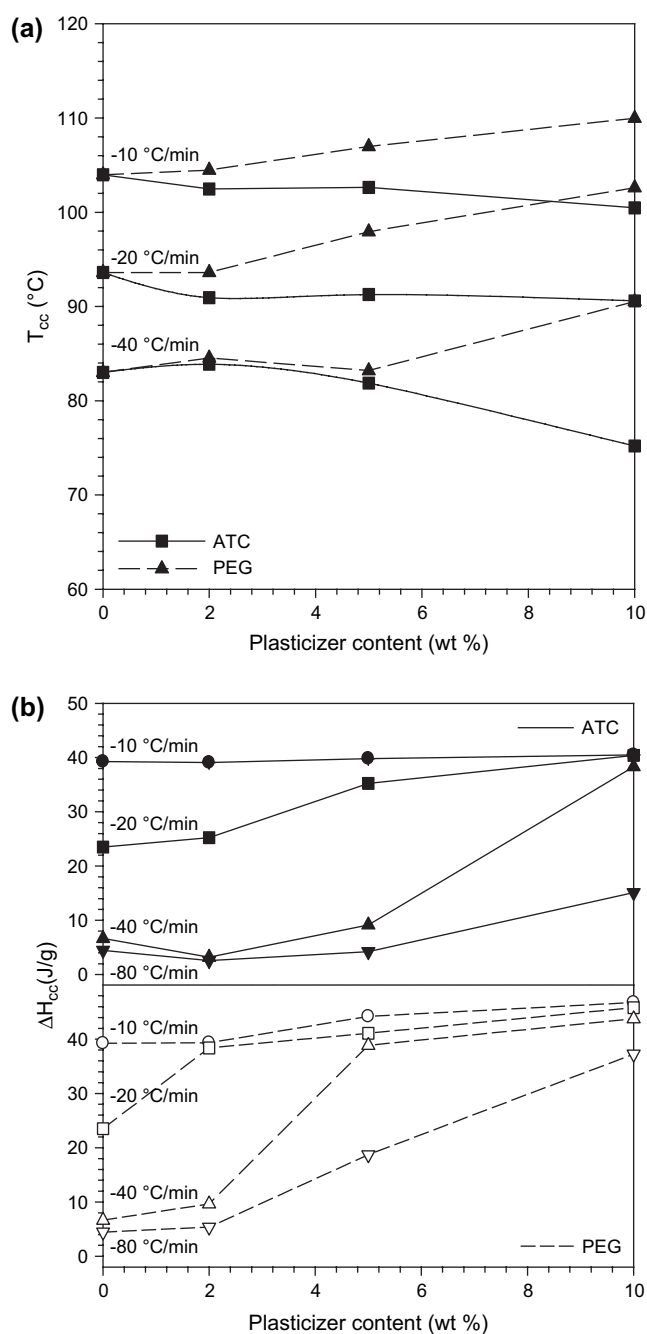
3.3. Isothermal crystallization kinetics

The addition of plasticizers and nucleating agents into PLA was also investigated in terms of half-time for crystallization under isothermal conditions at temperatures ranging from 70 to 130 °C. At fixed temperatures, the degree of crystallinity was followed as a function of time. The degree of crystallization X_t was expressed relative to the maximum achievable crystallinity level, thus $X_t = \Delta H_t / \Delta H_\infty$, where ΔH_t corresponds to the partial area of the DSC curve between the onset of crystallization at time t and ΔH_∞ is the melting enthalpy integrated between the onset until completion of crystallization.

The crystallization half-time $t_{1/2}$ is defined as the time required to reach half of the final crystallinity. Fig. 6 presents the half-time $t_{1/2}$ as a function of the crystallization temperature. Half-time curves typically show a minimum at a temperature T_{opt} defined as the optimum crystallization temperature. The pure PLA has a very slow crystallization and the minimum crystallization half-time is around 40 min at an optimum temperature around 100 °C. The addition of 1% talc effectively decreases the crystallization half-time to 90 s. In presence of 5% plasticizer with 1% talc, the minimum $t_{1/2}$ is reduced to 70 s for ATC and to less than 60 s in the case of the PEG plasticizer. The crystallization window is also widened, especially in the lower temperature range. At $T < T_{opt}$, crystal growth is the controlling factor in determining the overall crystallization rate. Therefore, it is expected that the
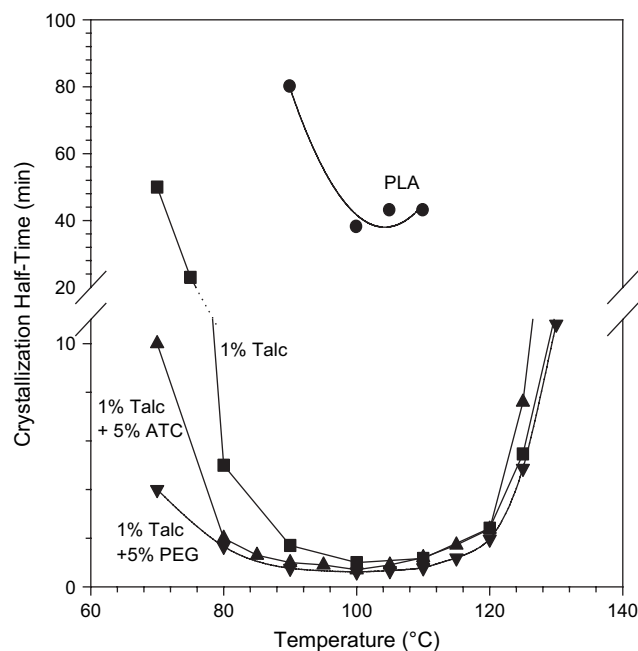
Fig. 6. Isothermal crystallization half-times for PLA, PLA with 1% talc, with 1% talc and 5% ATC, and with 1% talc and 5% PEG.

increased PLA chain mobility in presence of plasticizers will have a greater impact in the lower temperature range. In the higher crystallization temperature range, the addition of the PEG did not lead to significant $t_{1/2}$ changes while the addition of ATC lead to a slight increase at 125 °C. The isothermal data indicate that the PEG is a more effective plasticizer for PLA and therefore agrees with the non-isothermal data presented above.

3.4. Crystallinity development in molding conditions

There are two major differences in the crystalline development in polymer molding conditions compared to thermal analysis conditions. The first one is that the polymer is crystallizing during or right after it has been sheared and oriented by the flow. The polymer flow is known to potentially increase the nucleation process since bundles of highly oriented polymer chains can act as nuclei unto which secondary crystals grow in the direction perpendicular to flow (e.g. shish-kebab crystallization mechanism). The second major difference is the much higher cooling rate found in molding processes compared to those that can be imposed in a thermal analysis apparatus. The polymer is typically cooled from its melt processing temperature down to the mold temperature within seconds and thus the cooling rate is in the order of 10^3 °C/min rather than in the 10–100 °C/min range used in conventional thermal analysis. Since the enhanced nucleation rate and faster quenching have opposite effects that are difficult to actually quantify, it is interesting to investigate the crystallization development upon molding of the plasticized and nucleated formulations.

The crystallinity was probed after molding 3.1 mm thick bars using various conditions. In the 20–40 °C mold

temperature range, a cycle time of 30 s was sufficient to get quality parts that were cooled below PLA's glass transition temperature and that did not deform during ejection from the mold. Molding at 50–60 °C was difficult and parts were distorted during ejection because the parts were too close to the PLA's T_g and at the same time too cold to generate significant crystallinity. In the 70–100 °C temperature range, quality parts can be produced again but only for molding cycles greater or equal to 60 s which corresponds to the time required to develop sufficient rigidity through crystallization in the molded parts prior to ejection. Fig. 7 presents the crystallinity developed in the PLA formulation comprising 5% ATC and 1% talc. An S-shaped curve was observed with a low crystallinity level developed at temperatures below 50 °C and significant crystallinity developed in the high mold temperature region. In the high mold temperature region, the use of molding cycles of 60 or 90 s did not lead to significant changes in crystallinity levels since the material had crystallized up to its maximum level. Fig. 8 presents the effects of PEG or ATC plasticizer content on crystallinity developed for the PLA formulations with 1% talc. At 30 °C mold temperature, the samples were all nearly amorphous. At 80 °C molding temperature, the formulations developed substantial crystallinity. The crystallinity increased from 30 to 40 J/g, as the plasticizer content was increased to 5% and then reached a plateau. There was no obvious difference between the crystallinity developed with PEG or ATC plasticizers.

3.5. Tensile mechanical properties

Plasticization decreases the glass transition temperature and generally reduces the tensile modulus and tensile strength of
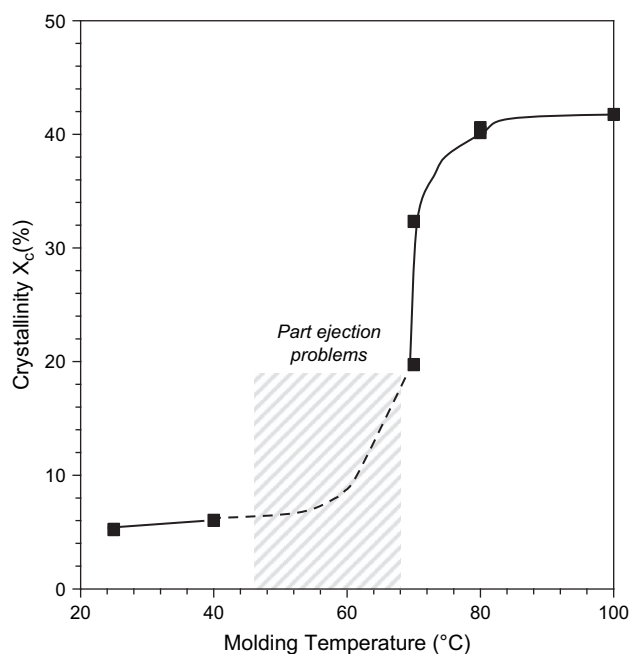

Fig. 7. Effect of molding temperatures on crystallinity (X_c) developed for PLA with 5% ATC and 1% talc.
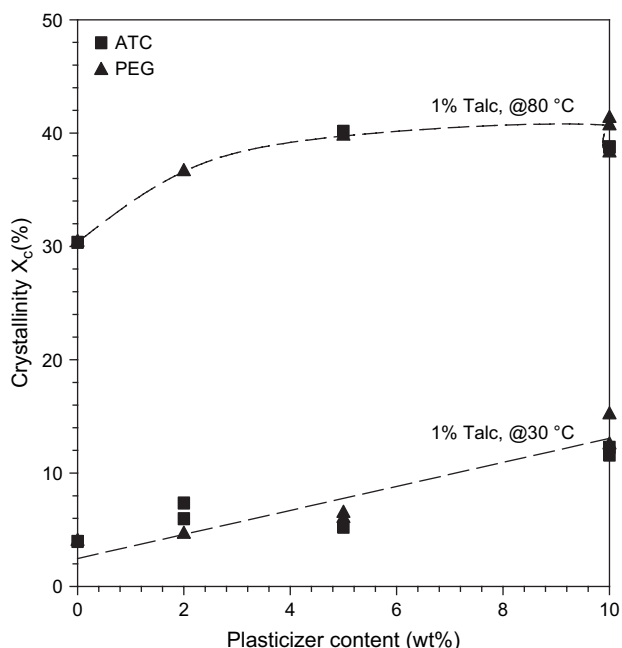
Fig. 8. Effect of plasticizer content on crystallinity developed at 30 and 80 °C mold temperatures.

amorphous polymers. However, in the case of slowly crystallizing polymers such as PLA, the increase in crystallinity due to enhanced chain mobility can partially or completely offset the plasticization effect. To investigate the interaction between plasticization and crystallization, the neat PLA and the formulations with plasticizers and/or talc were injection molded at 30 and 80 °C to generate nearly amorphous and fully crystallized sample, respectively. Table 1 presents the tensile modulus, strength and elongation along with the achieved crystallinity. The amorphous PLA presented high tensile modulus and tensile strength at 3.7 GPa and 70 MPa, respectively, and a relatively low elongation at break, around 5%. It was not possible to prepare fully crystallized neat PLA but formulation comprising as little as 1% talc could be fully crystallized when using a high mold temperature. Surprisingly, the tensile properties of these crystallized samples are similar to those of the amorphous neat PLA. It has been postulated that this absence of effect is due to the weak linkage between the amorphous and crystalline phases of PLA [33]. A second observation concerns the effect of the plasticizer. In absence of talc, the molded samples were nearly amorphous regardless of the plasticizer contents or molding temperature. For 2–5% ATC plasticizer concentration, the modulus was nearly unchanged and dropped only to 3.2–3.3 GPa when 10% ATC was added. Tensile strength dropped more steadily with plasticizer content with values dropping to 50–53 MPa at the 10% ATC level. The elongation was nearly unaffected at these plasticizer levels and remained below 10%. The sole effect of PEG (in absence of talc) was not investigated but it could be expected to follow similar trends. The next important observation concerns the effect of simultaneous addition of plasticizer and of the talc, nucleating agent. In this case, the

mold temperature significantly affected the crystallinity. All these formulations had a low crystallinity, below 15% when injected in a mold held at 30 °C. In this case the properties were similar to those of the plasticized formulations without talc as expected from their similar crystallinity levels. When mold temperatures of 80 °C were used, the samples were all close to being fully crystallized and in this case a peculiar phenomenon was observed. The tensile data for 2 and 5% plasticizer were similar to those reported for the more amorphous samples of similar plasticizer level, but suddenly at the 10% plasticizer level the modulus and tensile strength dropped almost by a factor of 2. Conversely, the elongation at break increased dramatically to 40 and 70% for 10% PEG and ATC, respectively. Since the plasticizer cannot be included within the crystals, a possible cause for this dramatic change can be the expulsion of the plasticizer from the crystallizing regions which in turn will increase the local plasticizer concentration in the amorphous regions. Prior work in ATC and PEG-plasticized amorphous PLA formulations showed that a dramatic ductility increases occurred only when at least 15% ATC [27] or 20% PEG [20] were used. In our case, the expulsion of the plasticizer out of the crystallizing regions that accounts for around 40% of the volume, can push the local plasticizer concentration in the amorphous regions in this critical concentration range.

3.6. Thermal resistance

As discussed above, the development of a significant PLA crystalline phase does not change dramatically the room-temperature tensile properties (other than at the 10% plasticizer level). The main purpose of developing crystallizable formulations, however, is to increase the temperature resistance of PLA. It is expected that crystallized formulations can withstand a given load up to a higher temperature since the crystalline regions should maintain material stiffness past the glass transition temperature of the amorphous phase. To investigate this topic, injection molded bars were subjected to dynamic mechanical thermal analysis (DMTA) in the 0–180 °C range. Fig. 9 presents the storage modulus E' as a function of temperature for neat amorphous PLA control and PLA formulations comprising 1% talc with 2, 5 and 10% PEG that are injected at 30 and 80 °C. For the pure PLA samples injected at 30 and 80 °C, the modulus exhibited similar behaviors: a long plateau up to the glass transition followed by a dramatic drop. The samples containing 1% talc and 2, 5% and 10% PEG injected at 30 °C, showed a similar behavior. However, for the same formulations injected at 80 °C, a similar plateau was observed but the modulus dropped less rapidly past the T_g showing the benefits related to the presence of the crystalline phase. At 10% PEG, the modulus starts dropping immediately at the start of the test (0 °C), probably due to the high local plasticization of the amorphous phase described earlier which reduced the T_g more significantly than in a fully amorphous sample. However, at higher temperatures, $T > 60$ °C, even the 10% PEG formulation has a higher modulus than the amorphous PLA control. It is noteworthy that it is possible

Table 1
Tensile modulus, strength and elongation at break (E, σ, ε_b) and crystallinity as a function of formulation and molding temperature

Plasticizer (wt%)	Talc (wt%)	Mold temperature (°C)	%X_c	Tensile properties, average (STD)		
				E (GPa)	σ (MPa)	ε_b (%)
0	0	30	6	3.68 (±0.13)	69.2 (±0.41)	6.0 (±0.29)
		80	14	3.70 (±0.10)	70.2 (±1.09)	5.8 (±0.32)
0	1	30	4	3.79 (±0.12)	63.9 (±0.77)	7.5 (±0.63)
		80	30	4.03 (±0.39)	67.7 (±0.71)	4.7 (±0.61)
2% ATC	0	30	<5	3.49 (±0.07)	64.3 (±0.68)	8.8 (±1.78)
		80	<5	3.54 (±0.24)	68.0 (±0.61)	6.0 (±0.31)
5% ATC	0	30	7	3.46 (±0.05)	57.8 (±1.32)	5.2 (±0.34)
		80	12	3.62 (±0.16)	59.2 (±1.94)	4.6 (±0.56)
10% ATC	0	30	<5	3.15 (±0.08)	50.1 (±0.28)	6.1 (±1.30)
		80	<5	3.32 (±0.17)	52.6 (±0.59)	4.6 (±0.07)
2% ATC	1	30	7	3.65 (±0.04)	60.1 (±0.18)	10.6 (±2.42)
		80	22	3.80 (±0.39)	65.4 (±0.84)	6.8 (±0.45)
5% ATC	1	30	5	3.59 (±0.07)	55.4 (±0.59)	9.0 (±3.34)
		80	36	3.75 (±0.21)	60.9 (±0.89)	5.3 (±1.39)
10% ATC	1	30	12	3.22 (±0.09)	47.3 (±0.98)	6.5 (±4.94)
		80	39	2.16 (±0.11)	34.5 (±0.37)	73.9 (±24.0)
2% PEG	1	30	5	3.70 (±0.14)	60.5 (±0.76)	10.5 (±4.61)
		80	37	4.23 (±0.02)	67.8 (±0.77)	6.2 (±1.88)
5% PEG	1	30	6	3.56 (±0.10)	54.5 (±0.96)	9.1 (±7.02)
		80	40	3.61 (±0.07)	53.8 (±0.28)	9.5 (±6.29)
10% PEG	1	30	14	3.02 (±0.07)	44.8 (±0.97)	39.9 (±37.2)
		80	41	2.39 (±0.05)	37.3 (±0.19)	40.4 (±14.6)

to produce a more ductile plasticized PLA formulation that yet has greater temperature resistance than unmodified PLA. Fig. 10 shows the temperature dependence of the loss modulus E'' for the same materials. For the amorphous samples, the E'' peaks shifted from 60 to 44 °C, as the PEG content in PLA was increased to 10%. For the crystallized samples, the E'' peak position did not change much in the 0–5% PEG range. At

10% PEG level, the peak was shifted down by only 8 °C, much less than that for the amorphous materials. The peaks were broader and weaker than those for the amorphous control. This broadening of the E'' peak may indicate a wider distribution in the range of PLA chain mobility. The PLA chains in the vicinity of crystalline phase have lower mobility and thus exhibit a higher T_g. In the amorphous zones, higher local
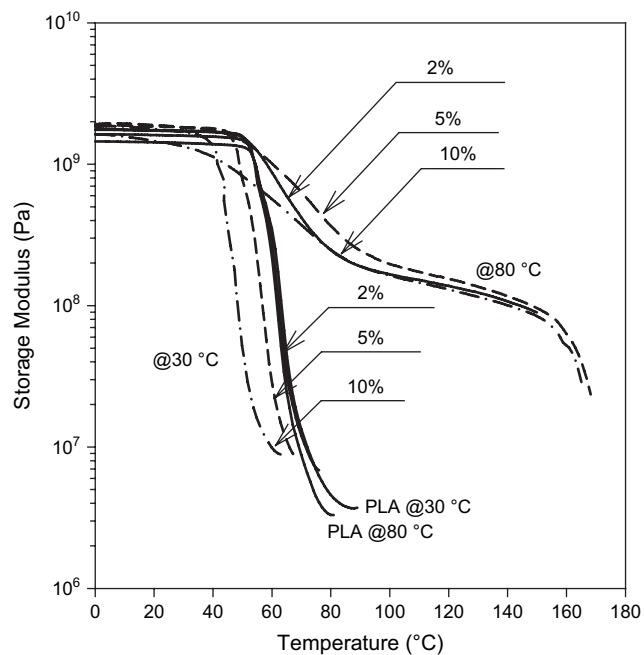

Fig. 9. Effect of temperature on the storage modulus for PLA control and for formulations comprising 1% talc with 2, 5 and 10% PEG, molded at 30 and 80 °C.
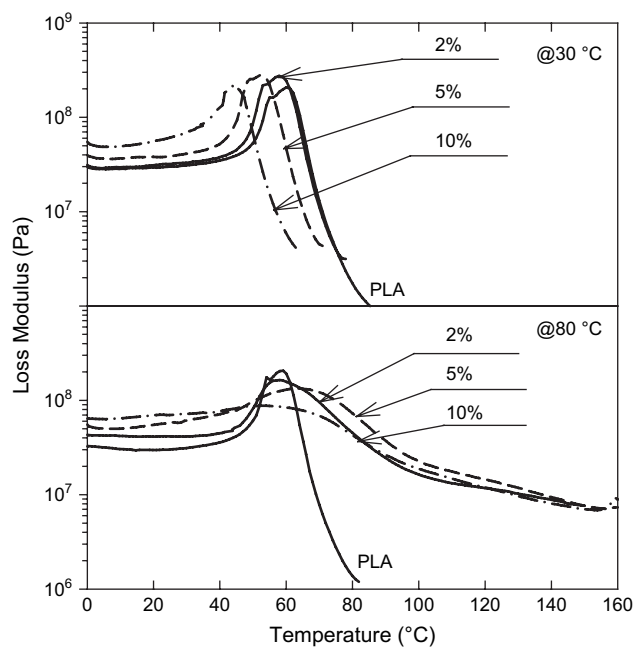

Fig. 10. Effect of temperature on the loss modulus for PLA control and for formulations comprising 1% talc with 2, 5 and 10% PEG, molded at 30 and 80 °C.

Table 2
Temperature resistance as a function of formulation and molding temperature

Plasticizer (wt%)	Talc (wt%)	Mold temperature (°C)	$\%X_c$	E'' Peak (°C)	tan δ Peak (°C)	T (°C) at 0.1 GPa	T (°C) at 0.3 GPa
0	0	30	6	60.0	65.1	72	59
		80	14	59.1	64.1	69	58
2% PEG	1	30	5	57.9	64.1	62.	59
		80	37	58.0	68.1	144	71
5% PEG	1	30	6	52.0	59.1	57	53
		80	40	63.1	77.1	143	78
10% PEG	1	30	14	43.7	50.1	48	45
		80	41	52.0	73.1	140	68

plasticization caused by the segregation effects described above are lowering the T_g below the expected value, thus expanding the E'' peak to a lower temperature range. The E'' peak broadening has also been reported for thermally annealed PEG-plasticized PLA films [21].

To compare the DMTA data obtained for different formulations and molding temperatures, we have quantified the heat resistance by determining the temperature corresponding to E' at levels of 100 and 300 MPa and have reported these data in Table 2. For a given stress or modulus level, the higher temperature corresponds to a higher temperature resistance. For PLA, at E' level of 100 MPa, the temperature determined by this method was around 70 °C, and this value drops by 25 °C upon addition of 10% PEG in amorphous samples injected at low temperature. In nucleated/plasticized crystalline formulations, however, the temperature resistance was increased to 140 °C, showing an important improvement over the amorphous controls. For an E' of 300 MPa, the temperature resistance was above 70 °C for the crystallized samples, compared with 59 °C for amorphous PLA and 45 °C when 10% PEG was added. Interestingly, the highest E' was obtained using 5% PEG. This level was sufficient to generate fully crystallized materials. Further PEG addition thus only contributes additional plasticization of the amorphous phase.

4. Conclusions

Crystallization of PLA in presence of nucleating agents and plasticizers was investigated using isothermal, non-isothermal and actual polymer processing conditions. It was found that talc was an effective nucleating agent while calcium lactate and sodium stearate had little or no nucleating ability. Polyethylene glycol (PEG) and acetyl triethyl citrate (ATC) were shown to be efficient plasticizers that increased the achieved crystallinity even at high cooling rates when used in combination with talc. The crystallization rate of the developed formulation was sufficient to obtain fully crystallized parts in an injection molding cycle. This required, however, the use of hot molds in the 70−100 °C range. The room-temperature tensile mechanical properties were only slightly affected by plasticizer content and crystalline content when 0, 2, 5% plasticizer was used. In fully crystallized formulation that contained 10% plasticizer, the ductility of the material increased dramatically. This effect was explained by a high plasticizer concentration in the amorphous phase. In all cases, the crystallized PLA formulations showed higher temperature resistance than the unmodified PLA controls.

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