The effect of polymer molar mass and silica nanoparticles on the rheological and mechanical properties of poly(E-caprolactone) nanocomposites

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ABSTRACT

The influence of nanosilica on the crystallization behavior, rheology and mechanical properties of poly(\textit{e}-caprolactone) (PCL) nanocomposites was investigated. It was found that the effect of nanofiller addition is dependent on the molar mass of the polymer matrix. For the higher molar mass matrix, a modest nucleation effect was observed, while in the lower molar mass matrices, this effect was absent. For the investigated range of filler contents, a modest increase in both modulus and ultimate tensile properties of the composites was observed. Lower molar mass matrices revealed voiding during deformation, which could be partly suppressed by the addition of nanofiller. The higher molar mass matrix showed no voiding in either the neat polymer or nanocomposite.

1. Introduction

Nanofillers of different type, shape, size and surface modifications have been added to a large variety of polymer matrices in order to improve properties such as the flow, crystallization behavior and mechanical properties. The results vary greatly, not only depending on the characteristics of the filler material, but also depending on the polymer under investigation. Anisotropic fillers, such as carbon nanotubes, graphene and different types of nanoclays, have shown to exhibit a great potential for the reinforcement of polymer matrices like poly(vinyl alcohol) (PVA) \cite{1,2} and poly(propylene) (PP) \cite{3,4}, while in other matrices the reinforcement was modest. Another interesting observation was that the addition of small amounts of nanosilica can decrease the viscosity of PP and poly(carbonate) (PC) without significantly altering the mechanical properties of the obtained material; a phenomenon that could be beneficial for the processing of high-molecular-weight polymers \cite{5,6}. These are rather surprising results, since in most cases the addition of solid particles to a polymer melt results in an increase of viscosity \cite{7}. The efficiency of nanofiller addition is highly dependent on the state of dispersion of the filler in the matrix, which is coupled to polymer–filler interaction and to the molecular weight of the polymer. The understanding of the underlying mechanisms of the different reinforcement effects remains difficult, since there are always many competing processes at play. In order to perform a systematic study of the influence of different material parameters like polymer molar mass or filler content, we have therefore chosen to restrict this research to one type of polymer matrix, that is, poly(\textit{e}-caprolactone) (PCL), and one type of nanofiller, that is, silica (SiO\textsubscript{2}).

PCL is a semicrystalline polymer that belongs to the polyester family and has been known for a long
time. It was first synthesized during the 1930s and was immediately considered of interest for biomedical applications, the advantages being its good processability with a low glass transition and low melting temperature, but above all, its biodegradability [8]. Outside the biomedical field it has, however, had few applications due to its mediocre mechanical properties. The development of PCL-based composite materials is a way to increase the applicability of the polymer outside the biomedical field and over the years several groups have therefore concentrated their research efforts on such composites. Due to the easiness to incorporate a large range of nanofillers in PCL matrices with fairly good dispersion [9–18], and its relatively straight-forward synthesis, it has also been used successfully as a model system for feasibility studies of grafting and other surface modifications of different nanofiller materials [14,19–25].

In this paper, we will report the rheology, crystallization behavior and mechanical properties of PCL of different molecular weights and compare this to the behavior of its nanocomposites incorporating silica nanoparticles. The local deformation behavior of the nanocomposites will also be investigated. Nanocomposites are prepared via a combined solvent casting and extrusion technique in order to ensure a good dispersion of the nanoparticles in all systems investigated. The silica nanoparticles used in this study are colloidal silica of the Stöber type and are of uniform size. The nanoparticles are used as received, which means that the particle surface is characterized by its hydroxyl groups. The prepared nanocomposites are characterized with several techniques and their resulting properties are linked to the state of dispersion and polymer–filler interaction.

2. Experimental methods

2.1. Materials

Three grades of poly(ε-caprolactone) (PCL) with different molecular weight where used in this study. CAPA® 6400 ($M_n$ 40 kg/mol), CAPA® 6500 ($M_n$ 50 kg/mol) and CAPA® 6800 ($M_n$ 80 kg/mol) from Perstorp Caprolactones (Perstorp, Sweden), hereafter referred to as PCL40, PCL50 and PCL80. Colloidal silica suspension (ORGANOSILICASOLTM) in toluene (TOL-ST) containing 40 wt% SiO$_2$ nanoparticles (10–15 nm) was obtained from Nissan Chemical Industries (Japan) and was used as received. As a solvent, toluene (C$_7$H$_8$) from Biosolve (The Netherlands) was used as received.

2.2. Sample preparation

The polymers were first dissolved in toluene followed by the addition of the colloidal silica suspension, also in toluene. The samples were left on a shaker for two nights in order to fully dissolve the polymer. Subsequently, the polymer solutions were poured into petri dishes and left to evaporate at room temperature (RT). After two nights of evaporation at RT the samples were dried in a vacuum oven under nitrogen atmosphere at 40°C. After drying, the samples were melt-compounded in a recirculating DSM X’plore 15MC micro-compounder operated at 200°C. The mixing was done at 75 rpm for 5 min in order to further improve dispersion. Samples for rheology, dynamic mechanical analysis (DMA) and tensile testing were compression molded by using a Dr. Collin hot press. The polymers were first melted at a temperature of 100–150°C and hot-pressed for 5 min at 100 bar. The cooling was done under pressure using recirculating cold water.

2.3. Characterization techniques

A Q500 thermogravimetric analyzer (TGA) from TA Instruments was used for the determination of the weight percentage of silica in the samples. Ten to 15 mg of sample was heated to 600°C at a rate of 10°C/min under nitrogen atmosphere. The dispersion of the nanoparticles was investigated with transmission electron microscopy (TEM). Ultrathin sections (70 nm) were microtomed at −100°C using a Leica UltraCut S/FCS microtome. The sections were placed on a 200 mesh copper grid with a carbon support. The sections were examined in a FEI Tecnai 20 transmission electron microscope, operated at 200 kV. Rheological measurements were performed using a stress-controlled AR-G2 rheometer from TA Instruments under nitrogen atmosphere. The matrix polymers were evaluated through measurements at 80, 90 and 100°C. First, amplitude sweeps were done at a constant angular frequency of 5 rad/s in order to determine the linearity region. Subsequently, frequency sweeps in the range of 100–0.1 rad/s at a constant strain of 10% were performed. For all samples, a 25 mm plate-plate geometry was used. Differential scanning calorimetry (DSC) measurements were performed on a Q1000 DSC from TA Instruments. 3–5 mg of sample was heated from RT to 100°C at a rate of 10°C/min and held at that temperature for 5 min. This was followed by a cooling step to −80°C, also at a rate of 10°C/min. This cycle was repeated twice. The melting temperature was determined from the maximum of the melting peak of the second heating run, while the crystallization temperatures (onset and maximum temperatures) were determined from the first cooling cycle. The degree of crystallinity was determined using a heat of fusion for 100% crystalline PCL of 136 J/g [26].
Mechanical properties were investigated using a Zwick 100 universal tensile tester. Small dumbbell-shaped samples with a total length of 30 mm, a width of 2 mm at the thinnest part and a thickness of 0.5 mm were cut according to ISO 527-2-1BB directly from compression-molded film samples. The test speed was 12 mm/min and the elastic modulus was determined from the slope between 3 and 5 Newton. For each composition, at least seven samples were tested.

For the evaluation of the mechanical properties of composite systems, many different micromechanical models have been proposed. One widely used practical model is the Halpin–Tsai equation [27]. According to this model the tensile modulus of a composite can be written as:

\[
\frac{E_{\text{comp}}}{E_{\text{matrix}}} = 1 + \frac{\zeta \eta \phi}{1 - \eta \phi} \quad (1)
\]

where \(E_{\text{comp}}\) is the modulus of the composite, \(E_{\text{matrix}}\) is the modulus of the polymer matrix, \(E_{\text{filler}}\) is the modulus of the filler, \(\phi\) is the filler volume fraction, while \(\zeta\) is a geometrical factor used to describe the influence of filler geometry on reinforcement that can be assumed to be 2 for a spherical filler with an aspect ratio of one. For the modulus of the neat polymer matrix, the average values of the modulus obtained from the tensile tests were used, and for silica, a value of 80 GPa was used [28].

The deformation mechanism of neat PCL and its nanocomposites was investigated via in situ small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) experiments performed at the Dutch–Belgian Beamline (DUBBLE) at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). An energy of 12 keV was used and the sample to detector distance was 7 m for the SAXS experiments and about 80 cm for the WAXD experiments. For recording the WAXD images, a FRReLoN 2000 detector (2048 x 2048 pixels) was used and for the SAXS images a 2D multewire gas-filled detector (512 x 512 pixels). The deformation of the samples was performed using a Linkam tensile testing unit that was placed horizontally in the beam. Tensile bars with a length of 30 mm, a thickness of 0.5 mm, and a width of 4 mm at the narrowest part of the half-moon-shaped indents were used in order to assure that the deformation always started from the same position (centered in the beam). The data collected during the experiments were treated using the image analysis program FIT2D. Prior to integration or plotting the 2D patterns, all images were corrected for background scattering and detector response. The integration of the patterns was performed using an in-house written MATLAB program.

3. Results and discussion

3.1. Morphology of nanocomposites

In a first step, the morphology of the prepared nanocomposites was assessed. In Figure 1, TEM images of the prepared samples are depicted. It can be observed that all samples display a relatively good level of dispersion, with only a few agglomerates present, even at high filler loadings. This presents an opportunity of studying the influence of filler content on the properties of the prepared nanocomposite while assuming a similar state of dispersion over the whole range of filler loadings investigated. This was unexpected, since it has been shown in literature that agglomeration occurs, particularly at high filler loadings [9,14] and that surface modification is needed to obtain good dispersions in PCL/silica nanocomposites [14]. From top to bottom in Figure 1, the influence of the molecular weight of the matrix can be seen. From the larger magnification (right) images, it appears that higher molar mass leads to improved dispersion. This can be explained by the higher shear forces developed during the extrusion compounding of these composites.

3.2. Rheological behavior

A profound knowledge of the melt properties is important for processing nanocomposite materials. In Figures 2(b) and 3(b), results from frequency sweeps at 100 °C are presented. In Figures 2(a) and 3(a), the loss and storage moduli are depicted as a function of angular frequency. The melt strength of the two polymer matrices is similar and the loss modulus is virtually unaffected by the filler addition. The higher loss modulus compared to the storage modulus implies a predominantly viscous behavior. The storage modulus is increased with the addition of filler and approaches the value of the loss modulus, which indicates a more solid-like behavior. The fact that the increase dominant in the lower frequency regime suggests the formation of a filler-network within the polymer melt that can be broken up at large deformations. This is also confirmed by the dynamic viscosity curves depicted in Figures 2(b) and 3(b). Neat PCL and nanocomposites with low filler content show a terminal behavior at low frequencies and a frequency-independent Newtonian plateau. With the increase in filler content, the
behavior deviates from Newtonian, and a significant increase in viscosity is observed. For the two PCL40 and PCL80 matrices, the magnitude of the viscosity change is different, but the trend is similar, with a deviation from Newtonian behavior starting around 3 wt% filler and solid-like behavior at 8 wt%. These results are in accordance with those reported by Li et al. [29] who found an onset of solid-like behavior at a filler loading between 7–9 wt%. Network formation has also been observed in other 0D filler systems. For instance, Zhang and Archer [30] investigated PEO/colloidal silica systems with and without surface modification. They found that network formation occurred at filler contents as low as 2 wt% and attributed this to the formation of an immobilized layer around the particle that increases

Figure 1. TEM images of different nanocomposites at two different magnifications (scale bar: left 0.2 μm, right 100 nm): (a) PCL40 + 1.2 wt% silica, (b) PCL40 + 5.9 wt% silica, (c) PCL40 + 1.2 wt% silica, (d) PCL50 + 4.6 wt% silica, (e) PCL80 + 1.3 wt% silica, and (f) PCL80 + 5.9 wt% silica.

Figure 2. Results from rheological experiments for PCL40. (a) The loss modulus (open symbols) and storage modulus (closed symbols) as a function of angular frequency. (b) The complex viscosity as a function of angular frequency. For all measurements, the temperature was 100 °C.
the effective size of the particle and to tie-molecules, that is, chains that are adsorbed on different particles forming bridges that contribute to a polymer–particle network. In contradiction to our work, they found that the loss modulus also increased with increasing filler content and that increased molecular weight had a distinct influence on the storage modulus. In Figures 2(a) and 3(a), a very modest molecular weight dependency of the storage and loss moduli is observed. Network formation has also been observed in other PCL-based nanocomposites like PCL/carbon nanotube (CNT) composites [13] and PCL/attapulgite composites [31], with one difference that the onset of network formation occurred at lower filler contents in those composites. This can be attributed to the higher aspect ratio of these fillers, since fillers with a higher aspect ratio need fewer contact points for the formation of a solid network. Another difference with these higher aspect ratio filler systems is that the formed networks are more robust and higher plateau values for the storage modulus are obtained.

3.3. Crystallization behavior

The onset temperatures of the crystallization peak ($T_{\text{onset}}$) for the different composite materials, measured during continuous cooling in a DSC, are represented as a function of filler content in Figure 4. Interestingly, it can be noted that for the lower-molecular-weight PCL matrices the trend is that the $T_{\text{onset}}$ decreases with increasing filler content (Figure 4(a,b)), while for the higher-molecular-weight matrices, the trend is an increase of the onset temperature with increasing filler content (Figure 4(c)). This means that if we calculate the nucleation efficiency with the method presented by Fillon et al. [32,33], we get negative numbers for the lower molecular weight matrices (PCL40, PCL50), that is, the addition of filler hampers nucleation, while in the higher-molecular-weight matrix (PCL80) a nucleation efficiency of about 20–25% is obtained. Avella et al. [14] found a similar decrease in crystallization temperature in PCL samples with a molecular weight of 60 kg/mol when the samples were prepared with unmodified silica, while other groups like Li et al. [9] have observed the same increase in crystallization temperature followed by a decrease in crystallization temperature at higher filler loadings than the ones presented here. An increase in crystallization temperature when silica particles were added have also been observed in both PP [34] and PLA [35,36]. With most filler types, the nucleation efficiency is however modest in the case of unmodified fillers [13,17,22,36] and increased when the fillers are surface treated [14,15,22,37]. The exception being CNTs which in most of cases display very high nucleation efficiencies of over 100% [36,38].

In Figure 5, the degree of crystallinity as a function of filler content is shown for the different nanocomposites. It is evident that samples with the lower molecular weight matrix have a higher degree of crystallinity than samples with a higher molecular weight. This is in accordance with literature and can be explained as follows. With an increase in molecular weight, the probability of adjacent re-entry is reduced, with chains more likely to re-enter further away or in neighboring lamellae, thereby forming tie molecules attached to more than one lamellae. This results in a constraint amorphous phase and interferes with the thickening of the crystalline lamellae [39]. Shorter chains are less likely to re-enter away from the growth surface of the growing lamellae, and will fold into more perfect crystals,
thus reaching a higher degree of crystallinity. The influence of filler addition on the degree of crystallinity is quite apparent. The degree of crystallinity decreases with increasing filler content for all matrix materials investigated. Keeping in mind that the viscosity is increasing with filler content, this can be explained in terms of chain mobility. Filler addition decreases mobility in the system as the fillers act as physical barriers, thereby decreasing the possibility for a chain to arrive at a growth front, decreasing the overall degree of crystallinity.

The crystallization behavior was also studied via in situ SAXS and WAXD experiments at the DUBBLE beamline at the ESRF in Grenoble, France. In Figure 6, the integration of the 2D SAXS images after nonisothermal crystallization upon cooling at a rate of $10^°C/min$ are presented. The presented integrations are performed on 2D images that were recorded once crystallization was finished. We can observe a slight shift in the maximum of the shoulder with increasing molecular weight. The long period $L$ is inversely proportional to the maximum of the scattering vector $q$ and can be calculated by $L = 2\pi/q$. For PCL40 and PCL80, it is 15.3 and 14.3 nm, respectively. The long period gives the distance between adjacent crystalline lamellae, which means that it comprises the lamellar thickness and the thickness of the amorphous phase in-between the lamellae. Knowing the volume percent of the two different phases, the lamellar thickness can be calculated according to $L = x_{\text{vol}}L$ [39]. Using literature values [40] for the density of the different phases ($\rho_c = 1.187\,\text{g/cm}^3$ and $\rho_a = 1.094\,\text{g/cm}^3$), the lamellar thickness $L_c$ could be estimated to 6.6 and 5.3 nm for PCL40 and PCL80, respectively. This implies that a higher molecular weight leads to the development of thinner lamellae. This can best be explained by a slower diffusion of polymer chains to the crystallization front due to the higher viscosity of the higher-molecular-weight samples. The silica particles scatter intensively in the low $q$-value region, and therefore, the peak related to the long
period of the polymer is only observed in the samples with relatively low filler content. At this low filler content, the long period remains similar, which indicates that the addition of small amounts of filler does only affect the degree of crystallinity and not the morphology of the spherulites. However, based on the SAXS results, no conclusion can be drawn regarding the influence of high filler loadings. A quick calculation of the interparticle distance for a nanocomposite with 5 wt% of 10-15 nm large silica particles gives an estimate of 17–25 nm, which is close to the length scale of the long period, indicating that also the morphology of the spherulites could be affected at the highest filler loadings.

3.4. Mechanical properties

The mechanical properties of the different molecular weight matrices together with their nanocomposites were investigated using tensile testing. Furthermore, the local deformation mechanism was studied using in situ X-ray scattering/diffraction experiments performed at the DUBBLE beamline at the ESRF in Grenoble, France.

3.4.1. Tensile properties

In Figure 7(a), the Young’s modulus obtained from the tensile tests is presented as a function of filler content for the three PCL matrices. For the neat matrix materials, the modulus follows the same trend as the degree of crystallinity with a higher modulus for the samples with the lower molecular weight. To predict the reinforcement efficiency in a composite material, the Halpin–Tsai model can be used [27]. The dotted lines in Figure 7(a) represent predictions from the Halpin–Tsai model for a composite material assuming that the silica particles have an aspect ratio of one (spherical). At low filler
contents, the prediction is rather accurate and only minor increases in modulus with increasing filler content are observed. At the highest filler content, the measured values are significantly lower than the predicted values in samples prepared with the lower-molecular-weight matrices. A prerequisite for the validity of the Halpin–Tsai composite model is that the properties of both phases are the same as they would be if the other phase was not present [41]. In the low-molecular-weight matrices a decrease in both crystallization temperature and degree of crystallinity is observed upon increasing the filler content. As already discussed, the modulus of a semicrystalline polymer depends on the degree of crystallinity and a decrease in crystallinity will therefore lead to a decrease in the modulus of the composite matrix which offsets the increase from filler addition. A deviation from a theoretical prediction is therefore not unexpected. The difference between the different molecular weight samples can most likely be attributed to differences in the level of dispersion of the nanofiller in the matrix. The higher viscosity of the higher-molecular-weight samples accounts for stronger shear during extrusion compounding which leads to better dispersion. It is expected that by increasing the filler content even further, a deviation from theoretical values will also be observed for the high-molecular-weight PCL80 matrix. This was indeed observed by Li et al. [29] who showed that the modulus was increasing with the filler content up to a silica content of about 7 wt% and thereafter started to decrease.

In Figure 7(b), the yield stress of the different composites is presented. In the lower-molecular-weight matrices, PCL40 and PCL50, the yield stress is decreased with increasing filler content, while for the PCL80 matrix, it remains fairly unaffected. This is in line with the results of the crystallization experiments showing a decrease in crystallization temperature and degree of crystallinity for the low-molecular-weight samples, PCL40 and PCL50, while PCL80 shows an increase in crystallization temperature and no significant changes in the degree of crystallinity.

The elongation at break and the ultimate tensile strength of nanocomposites based on the PCL40 matrix are shown in Figure 8. This is the only matrix in which these values could be determined properly. For the other matrices, slip in the clamps led to an overestimation of the tensile parameters. The tensile properties of a composite can be affected in different ways by the addition of rigid particles. Weakening and embrittlement of the polymer matrix and early failure due to stress concentrations around particles is a known problem with conventional micron-sized fillers and in agglomerated nanocomposite systems [42]. However, small enough particles can also toughen the polymer matrix by contributing to void formation via debonding from the matrix and act as physical barriers to crack growth [43]. As an example Ash et al. showed that PMMA changed from a brittle fracture mode to ductile behavior when 2.2 wt% nanosized alumina particles were added [44]. TEM pictures showed clear void formation around the particles, indicating that debonding from the PMMA matrix occurred. In another interesting example of nanoparticles toughening a polymer matrix, different types of silica were added to an immiscible blend of PCL and PLA [45]. In this example, the preferential migration of silica particles to the interphase of the blend changed the morphology of the blend but also facilitated cavitation at the interface, resulting in a greatly enhanced toughness of the blend. In Figure 8, an initial increase of the ultimate tensile strength followed by a decrease at the highest filler loading is observed. These results are in agreement with those of Li et al. who also found a decrease in tensile strength at about 3 wt% silica loading [29]. This decrease at high filler loadings can be attributed to agglomeration of the silica nanoparticles while the increased tensile strength and elongation at break at lower filler content can be attributed to suppressed void formation in the polymer matrix. In the following paragraph this hypothesis will be discussed in more detail.

3.4.2. Deformation mechanism

The deformation behavior of the nanocomposites was evaluated by performing in situ SAXS and WAXD measurements at the DUBBLE beamline at ESRF using a Linkam tensile tester. A typical example of a force-displacement curve obtained during the measurement is presented in Figure 9. The samples show an initial elastic deformation, yield and postyield behavior that involves the
development of a stable neck. The fact that the measurements are interrupted before strain hardening sets in is due to the limitations of the measurement equipment.

The 2D WAXD images recorded during the tensile deformation are shown in Figure 10. Except for the image taken at time zero, all the presented images are obtained beyond the yield point, during neck formation and propagation. Images were also recorded prior to necking but they all showed the same isotropic rings as the undeformed samples and are therefore omitted in view of space. Prior to deformation, isotropic, so-called Debye–Sherrer rings are observed. Once the samples have passed through the yield point, a preferred orientation, characterized by intense regions at the meridional, are observed. During the course of the necking process, these regions become smaller and more intense, indicating that more crystals orient in the preferred direction. In a dumbbell-shaped tensile bar, the necking can be initiated at any point along the bar and the time we measure is thus not a time characteristic for the deformation, but it is also influenced by the time that it takes for the neck to propagate into the beam position from the random point where it was initiated. The use of tensile bars with half circle-shaped indents assures that differences in intensity of the WAXD patterns can be used to detect differences in the rate of the reorganization between the different samples. However, from the direct observation of the 2D WAXD images, no influence of either the molecular weight or the filler addition on the...
deformation behavior of the crystalline phase can be observed. The lack of changes in the crystalline structure confirms that the nanoparticles are located in the amorphous regions between the crystalline lamellae and not in the crystals themselves.

Figure 11. SAXS images recorded during in situ deformation of PCL40 (top two rows), PCL40 + 1 wt% silica (3rd and 4th row), PCL80 (5th and 6th row), and PCL80 + 1 wt% silica (bottom two rows). The deformation rate was 1 mm/min. The deformation direction is in the horizontal direction in the images.

The SAXS images recorded during the deformation are presented in Figure 11. Prior to deformation, an isotropic ring can be seen in all samples. This ring corresponds to the average distance between two adjacent lamellae in the crystalline morphology of stacked lamellar crystals. Upon
deformation, streaks appear at the meridional close to the beam stop. These streaks originate from the formation of voids. On further deformation, the isotropic ring from the nonoriented lamellar crystals first changes into an elliptical shape with a rather even distribution of the scattered intensity. At some point, the elliptical shape disappears and arcs appear at the equatorial. These changes in scattering pattern correspond to a break-up of the spherulitic structure and reorientation of the lamellae in the drawing direction. In contrast to the WAXD images, a difference can be observed between samples of different molecular weight. In the samples with the higher molecular weight, only very small streaks can be observed, indicating that void formation is less prominent. The tensile deformation of PCL was also studied in detail by Jiang et al. [46] and they showed that samples crystallized at different temperatures, thus possessing different morphologies, revealed similar differences in SAXS pattern. Samples crystallized at low temperature had smaller and thinner meridional streaks while samples crystallized at higher temperature showed larger streaks. This was attributed to the difference in crystal perfection between the different samples.

The two sets of images situated at the 3rd and 4th and bottom rows of Figure 11 correspond to nanocomposites with 1 wt% silica. Due to high electron density differences, the silica nanoparticles scatter intensively at small angles. Therefore, only the samples with 1 wt% could be evaluated. For samples with higher silica content, the silica scattering completely dominates the 2D images. The deformation behavior of the nanocomposites is similar to that of neat PCL. Interesting to note is also that in the nanocomposites with a low-molecular-weight PCL matrix the meridional streaks that correspond to void formation are less intense compared to the neat polymer, which might imply that void formation is suppressed in these nanocomposites.

In order to gain more quantitative information on the underlying mechanism of deformation, the 2D SAXS images were integrated in the equatorial and meridional directions. The resulting curves, showing the intensity as a function of Q-value, were divided in two zone; a zone close to the beam stop (0–2 nm⁻¹), where the scattering can be attributed to either voids or the silica particles, and a zone covering the zone corresponding to the scattering from the polymer crystals (3–7 nm⁻¹). The maximum intensity and the corresponding q-value of each zone were then plotted as a function of the deformation (Figure 12). These plots clearly show the difference between the PCL40 and PCL80 grades. In the lower-molecular-weight sample, extensive voiding occurs, which is absent in the sample of higher molecular weight. The integrated data also clearly shows a reduction in intensity resulting from void formation when silica was added to the low molecular weight sample.

As already explained, the streaks observed close to the beam stop in neat PCL40 are attributed to the formation of voids during deformation. During the initial stages of deformation, elastic deformation of the polymer occurs and the resulting SAXS image has an elliptical shape, slightly elongated at the meridional. Just before, or at the yield point, voiding perpendicular to the drawing direction is often observed in PCL and in the SAXS patterns these voids will show up at the equatorial close to the beam stop [47]. These equatorial lobes are not clearly visible in the scattering patterns presented in Figure 11. However, a small increase in scattering density, followed by a rapid decrease at the yield point is observed in the integrated data. Upon softening, the constraints on the voids are released and they can start to grow in the direction of drawing, which in the SAXS images results in a shift of the scattering intensity to the meridional direction. This can clearly be observed in both the 2D images and the integrated data. Upon necking, the voids grow further in the direction of the deformation and in the SAXS patterns intense streaks at the meridional are observed. This voiding takes place in the amorphous phase in between the lamellae inside the spherulites or at boundaries between different spherulites. It has been shown that increasing the molecular weight can decrease the extent of voiding, probably due to a more coherent and entangled amorphous structure [48]. Moreover, it was shown that semicrystalline polymers with large, perfect spherulites are more prone to void formation than polymers with small, imperfect spherulites [47]. This was explained by the fact that in less perfect structures the plastic deformation of the crystals occurs sooner, at a lower stress, than voiding. In larger, perfect structures, the onset of plastic deformation of the crystalline structure occurs at higher stresses and voiding sets in earlier. Based on this information, the following deformation mechanisms are proposed for the presented systems.

PCL40 has a relatively low-molecular-weight, well-developed spherulites and a high crystallinity. The critical stress for void formation is therefore lower than the yield stress and extensive voiding occurs. PCL80 has a much higher molecular weight and does therefore contain less perfect crystals and a lower degree of crystallinity under the same crystallization conditions. The yield stress of this polymer is lower and, therefore, the crystals will start to deform plastically before voiding can occur. In Figure 12, it can be clearly seen that voids in PCL40
are formed prior to yielding, and that PCL80 is beginning to yield at smaller deformations.

Even though the addition of silica nanofillers does not change the crystalline structure of PCL it still introduces disorder into the spherulitic structure. Evidence for this can be found in the decrease in crystallinity with increasing amount of nanofiller. The result is a lower critical value for the onset of

Figure 12. Maximum intensities (left column) and corresponding Q-values (right column) plotted as a function of deformation. The values are obtained from integration of the 2D SAXS images. The black symbols correspond to the equatorial direction, while the red shows the meridional direction. The scattering represented by closed symbols can be attributed to the PCL crystals, while open symbols represent scattering close to the beam stop (voids or silica particles). From top to bottom: PCL40 (top row), PCL40 + 1 wt% silica (2nd row), PCL80 (3rd row) and PCL80 + 1 wt% silica (bottom row) are depicted.
yielding, and, as a consequence, the voiding process in the lower-molecular-weight PCL is suppressed. Moreover, voiding takes place in the amorphous phase in between the lamellae inside the spherulites or at boundaries between different spherulites and this is also where the silica nanoparticles are located. From the TEM images, it can be concluded that the dispersion of the silica nanoparticles in the PCL matrix is rather good. This means that the inter-particle distance, that is, the distance between two adjacent particles, is small and fairly uniform. This small and uniform inter-particle distance contributes to the suppression of voiding. Even if the formation of small voids occurs, cracks of a critical size do not have enough space to form and plastic deformation can occur in the matrix ligaments in between the nanoparticles. This is also the explanation for the unusually high elongation at break at low and intermediate filler levels. In the PCL of higher molecular weight, the formation of voids is already suppressed, which explains why no or little effect of the filler can be observed.

4. Conclusions

In this research, the influence of polymer molar mass and filler addition on the crystallization behavior, and rheological and mechanical properties of PCL/silica nanocomposites were studied. It was shown that an excellent level of nanoparticle dispersion could be obtained with the employed extrusion compounding method. The silica nanoparticles influenced the melt rheology of the polymer systems, increasing the viscosity and storage modulus. In addition, the crystallization behavior was also affected. The influence of filler addition on the crystallization temperature was molecular weight dependent. For the lower molecular weight–based nanocomposites, filler addition caused a decrease in crystallization temperature, while in the higher-molecular-weight systems, an increase in crystallization temperature with increasing filler content was observed. This difference may originate from the difference in crystallization behavior of the different PCL matrices. Lower-molecular-weight PLC can crystallize more easily and the addition of nanosilica only reduces the chain mobility in the system, imposing physical barriers onto the polymer chains. In the higher-molecular-weight PCL, the crystallization behavior of the neat polymer was slower as compared to the lower-molecular-weight systems and the addition of nanosilica provided some additional nucleation sites which increased the crystallization temperature in these materials.

The elastic modulus of the nanocomposites was increased upon the addition of small amounts of silica nanoparticles and the behavior followed Halpin–Tsai micromechanical predictions at low filler loadings (<4 wt%). At higher filler loadings, deviations from theoretical predictions were found which were attributed to agglomeration of the silica nanoparticles. The tensile strength and elongation at break were only measured for the PCL40-based nanocomposites and remained virtually unchanged with filler addition. All the samples deformed via localized yielding followed by stable neck formation. During necking, voids were formed in the lower-molecular-weight PCL matrix, while in the polymer of higher-molecular-weight voiding was not present. Addition of a few weight percent of nanosilica to the lower-molecular-weight matrix seemed to suppress void formation in the polymer, which resulted in an increased tensile strength and elongation at break.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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