Full Paper

Morphology and Crystallization of Bio-based Polyamide 56 Blended with Polyethylene Terephthalate^a

Yurong Yan^{1,2*}, Ali Gooneie^{2**}, HaixianYe¹, Lingli Deng¹, Zhiming Qiu¹, Felix A. Reifler^{2,3}, Rudolf Hufenus²

¹School of Materials Science and Engineering, South China University of Technology, Guangzhou, China, 510640

²Laboratory for Advanced Fibers, Empa, Swiss Federal Laboratories for Materials Science and Technology, Lerchenfeldstrasse 5, 9014 St. Gallen, Switzerland

³Center for X-ray Analytics, Empa, Swiss Federal Laboratories for Materials Science and Technology, Ueberlandstrasse 129, 8600 Dübendorf, Switzerland

Corresponding Authors: *yryan@scut.edu.cn; **ali.gooneie@empa.ch

Abstract. In this study, we attempt to promote bio-based polyamide 56 (PA56) as a sustainable candidate to replace commercial PA6 and PA66 when blended with polyethylene terephthalate (PET). Scanning and transmission electron microscopy of the blends with different PA56 contents reveal an immiscible morphology with an increase in the size of the dispersed domains by increasing PA56 content. The steady-state mixing torque of the kneader is decreased to half by adding 10 wt% of PA56 to PET. Further addition of PA56 gradually increased this torque but does not surpass the neat PET sample up to 30 wt% of PA56. As revealed by microscopic dissipative particle dynamics (DPD) simulations, this gradual

^a **Supporting Information** is available online from the Wiley Online Library or from the author.

increase is ascribed to the difficulty to disperse larger domains of PA56 in the thermodynamically undesired PET. The results confirm that PA56 has a lubricating effect in PET. Using polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD) techniques it is showed that PA56 acts as a nucleating agent in PET. This leads to the formation of numerous small crystals in the blends as opposed to several large crystals in the neat samples. The results encourage the use of PA56 biomaterial in combination with PET in products such as bicomponent segmented pie fibers.

Keywords: Polyamide 56, PET, Morphology, Crystallization, Dissipative particle dynamics

1. Introduction

Polyamide was first synthesized in the 1930s by Carothers at DuPont.^[1] In recent years, the depletion of fossil oil resources and their fluctuating prices on one hand, and fundamental research in microbiology and germ technology on the other hand,^[2] boosted the development of monomers derived from bio-based sources. Bio-based polymers are synthesized using e.g. carbohydrates of vegetable origin, or fatty acids, supported by biological, chemical and/or physical processes.^[3] Vegetable oils, commonly extracted from plants,^[4] represent one of the most promising sources for renewable chemicals used for the production of bio-polymers. This applies especially for triglycerides, which are the product of etherification of glycerol with fatty acids.^[5] Also diamine raw materials, used in the synthesis of polyamide, are increasingly substituted by bio-based products stemming from enzyme reaction and microorganism culture.^[6] In this respect, cadaverine (1,5-pentanediamine) is an important raw material for synthesizing bio-polyamides such as polyamide 54 (PA54) and polyamide 56 (PA56) (succinic acid/adipic acid and cadaverine).^[7] The production of cadaverine by renewable biomass (*C. Glutamicum*) is one of the most attractive biotechnological developments as an alternative to fossil resources.^[8]

As a viable bio-based alternative to polyamide 6 (PA6) and polyamide 66 (PA66), PA56 can be synthesized by direct polycondensation of 1,5-pentamethylenediamine obtained from L-lysine and adipic acid (see **Figure S 1** of the Supporting Information). With a glass transition temperature of approximately 55°C and a melting temperature of about 251°C, PA56 shows thermal properties and a heat resistance comparable to the commercially available PA6.^[9] Since PA56 has a higher amide group density than PA6, it has the potential to establish a denser network of hydrogen bonds between the polymer chains than PA6. Therefore, PA56 shows a much higher moisture regain compared with PA6,^[10] which makes it particularly attractive for some applications such as fibers giving them more comfort in wearability.

Moreover, PA56 also shows a higher dyebath exhaustion than PA6 during the dyeing process carried out with acid dyes.^[10] Overall, the bio-based PA56 has a good balance between chemical resistance, wear and abrasion resistance, mechanical, and thermal properties.^[11]

Considering all of its favorable properties and benefits, PA56 is a promising candidate to be processed separately or together with other polymers such as polyethylene terephthalate (PET). By using PA56 and PET, bicomponent fibers with a segmented pie cross section can be processed according to modern bicomponent spinning technology.^[12] Recently, we developed such splittable microstructures with bio-based PA56 and PET which can be later separated using either chemical or mechanical post-treatments, see **Figure 1**. The development of bio-based PA56/PET segmented pie fibers strongly depends on the compatibility between the two polymers. Therefore, the present study is mainly focused on this aspect. If the adhesive force between PET and PA56 is weak, the mechanical separation is viable to be carried out,^[13] otherwise chemical treatment must be used. Therefore, the compatibility of the co-processed polymers plays a key role in determining the splitting technique. Examples for the application of such PA56/PET fibers are microfiber fabrics used as wiping cloths (**Figure 1**), mops, towels, upholstery, apparel, rain- and sportswear. After use, such disposable products are often to be recycled for their reuse offers a sustainable processing. Currently the most common recycling process of plastics is the mechanical method which involves melting them down into pellets for further reutilization.^[14–17] Considering that PET is one of the most commonly recycled thermoplastic polymers, further investigations are necessary to understand the morphology developments in its blends with PA56. In this regard, compatibility with PET is of significance for PA56 as a substitute for PA6 and PA66^[18–20] to achieve suitable mechanical properties of products made from such blends.^[21–24]

Figure 1. (a) The schematic representation of segmented pie fibers from PA56/PET blends. (b) Microfiber fabrics based on bicomponent segmented pie fibers can have a variety of applications including cleaning of delicate surfaces where any scratches must be avoided. (c,d) The segmented pie fibers produced from PA56/PET blends in our pilot setups with different magnifications.

Even though the advantages of PA56 over its traditional substitutes are evident particularly from a bio-friendly perspective, the literature on its properties and behaviors is disappointingly scarce. In comparison, the morphology and crystallization behavior of PET blends with PA6 and/or PA66 are addressed in a number of studies.^[25–30] In order to answer these demands, we melt-blended bio-based PA56 with commercial PET and characterized their morphology and crystallization behavior. We employed a variety of characterization methods including differential scanning calorimetry (DSC), polarized optical microscopy (POM), scanning electron microscopy (SEM) and X-ray diffraction (XRD) among others to achieve a rich spectrum of experimental data. Furthermore, under-equilibrium blends morphology at the molecular level was investigated utilizing microscopic dissipative particle dynamics (DPD) simulations. All these information combined will provide a multiscale perspective into the morphological developments and crystallization behavior of the blends

during melt processing starting from a few angstroms, to a few nanometers, to several microns.

2. Materials and Methods

2.1. Raw Materials

PET pellets were provided by Zhuhai Yuhua Polyester Co., LTD. PA56 pellets were produced by Shanghai Kaisai Biotechnology Research and Development Center Co., Ltd., China. Formic acid (A.R) was purchased from Guangdong Xinning Chemical Factory, China.

2.2. Sample Preparation

PET and its blends with PA56 in wt/wt ratios of 90/10, 85/15, 80/20, and 70/30 were prepared by melt mixing in a torque mixer (PLASTI-CORDER, Brabender, Germany). Prior to melt blending, PET and PA56 pellets were dried separately in a vacuum oven for 12 hours at 130°C. The samples were blended at 270°C, with a rotor speed of 35 rpm. The total blending time was set to 15 min. After blending, all samples were cut into small pieces and dried in a vacuum oven for 10 hours at 110°C before further characterization.

2.3. Characterization Methods

2.3.1. Differential Scanning Calorimetry

DSC 204F1 (Netzsch, Germany) was used for differential scanning calorimetry (DSC) tests. Polymer samples of 5-10 mg were placed in aluminum crucibles, covered and compacted. First heating step was from 20°C to 300°C at a rate of 10°C/min, followed by 5 minutes isothermal stage at 300°C. The cooling step was from 300°C down to 20°C at 10°C/min,

followed by a hold at 20°C for 5 min. Finally, second heating was again ramped from 20°C to 300°C at a rate of 10°C/min.

For the non-isothermal crystallization kinetics tests, the instrument was calibrated periodically with an Indium standard to ensure reliability of the data. The sample weight was kept constant and the crystallization program for the first heating was from 20°C to 290°C at a rate of 10°C/min. Then, the temperature was maintained at 290°C for 5 min. The cooling step was from 290°C down to 20°C at different cooling rates of 3, 5, 10, 15 and 20°C /min.

To assess non-isothermal crystallization,^[31] the relative crystallinity X_T is determined by integrating the exothermal peaks during the non-isothermal scan at different crystallization temperatures (T_c) using equation 1,

$$X_T = \frac{\int_{T_0}^T (\frac{dH_c}{dT})dT}{\int_{T_0}^{T_\infty} (\frac{dH_c}{dT})dT} . \quad (1)$$

where, T_0 and T_∞ are onset and end of crystallization temperatures, respectively, dH_c is the variation of enthalpy, and dT is the change in temperature. The relationship between crystallization temperature T and crystallization time t , can be expressed by equation 2,

$$t = \frac{|T_0 - T|}{\phi} . \quad (2)$$

Here, ϕ is the cooling rate, and T_0 is the initial temperature when crystallization begins ($t = 0$). The half-time of crystallization $t_{1/2}$ is then defined as the time when 50% crystallization is obtained according to X_T - t curves.

2.3.2. Microscopy

For polarized optical microscopy (POM), PA56/PET specimens were cut into small pieces, fixed between microslide and coverslip, melted into a film at 280°C, and finally cooled down

to room temperature. Observation of the crystallization process was carried out on a hot stage polarized light microscope BX51-Plinkamthms 600 (Olympus, Japan) using the following conditions: heat up the specimens from room temperature up to 280°C at a speed of 20°C/min, maintain constant temperature of 280°C for 5 min, and cool down to 110°C at a speed of 12°C/min.

For scanning electron microscopy (SEM), etched samples of the blends were prepared as follows: samples were immersed for 48 and/or 96 hours in formic acid to dissolve the polyamide, followed by washing with distilled water to remove residual formic acid, and drying in vacuum oven for 10 hours at 90°C. For SEM analysis, specimens were attached to the sample holder with a conductive adhesive, and sputtered with gold. A Quanta 200 scanning electron microscope (FEI, Netherlands) was used with an accelerating voltage of 20 kV. The micro structure of blended PA56/PET was further examined by a transmission electron microscope (TEM) 2100F (Electron, Japan) with an accelerating voltage of 200 kV.

2.3.3. X-ray Diffraction

X-ray diffraction (XRD) was performed on a X-ray diffractometer X-pert PRO (Panalytical, Netherlands) at scanning speed of 5°/min and scanning range (2θ) from 5° to 90°, using a Cu anode, wavelength λ of 0.15418 nm, tube voltage 40 kV, and tube current 40 mA. The diffraction data were evaluated using the evaluation software BRUKER DIFFRAC.EVA (version 4.2., Bruker AXS, Karlsruhe, Germany). Powder diffraction intensities from literature data were calculated using Cryscon (version 2.0.3, Shape Software, Kingsport, TN, USA), a crystallography conversion utility.

3. Microscopic Simulations

Dissipative particle dynamics (DPD) was employed to investigate the microscopic equilibrium morphology of PA56/PET blends.^[32–34] DPD is a well-established coarse-grained simulation technique which has proved extremely valuable in the prediction of the morphological evolutions of soft matter on larger time scales than that accessible by classic molecular dynamics.^[35–37] The underlying principles of this method are described in details elsewhere and are not to be repeated here to preserve brevity.^[33,38–40]

In order to represent a flexible polymer chain, several DPD beads were linked by finitely extensible nonlinear elastic (FENE) springs with the potential of $U_{FENE}(r_{ij}) = -0.5 k_s r_0^2 \ln \left(1 - \left(\frac{r_{ij}}{r_0} \right)^2 \right)$ in which k_s is the spring constant, and r_0 is the maximum extent of the bond, and r_{ij} is the distance between the bonded beads i and j . These values were set to $50 k_B T / r_c^2$ and $0.7 r_c$, respectively, for all bonds in PET and PA56 chains with k_B representing the Boltzmann constant, T the simulation temperature, and r_c the force cut-off radius of the conservative forces in the DPD force field. Each two consecutive bonds were allowed to have any angle in order to preserve the flexibility of the chain. Since the molecular weights of both polymers were approximately the same, i.e. ~ 18 kg/mol,^[40,41] all PET and PA56 chains consist of a similar number of beads equal to 20 in our models. This degree of coarse-graining results in a unit mass m of 1.54×10^{-24} kg for each bead and a length unit r_c of 1.53 nm. The energy unit is $E = k_B T$ at $T = 543$ K, the same as the processing temperature. The time unit τ is 220 ns.

For all interactions between beads of the same type in the simulations, the maximum repulsion coefficients, a_{ii} , were set to $25 k_B T / r_c$. For interactions between beads of different types, Groot and Warren's approach was utilized to relate the excess repulsion parameter to

the Flory-Huggins χ_{ij} parameter as $a_{ij} \approx \frac{\chi_{ij}}{0.306} + a_{ii}$.^[32] Here, χ_{ij} is determined using the solubility parameters δ_i and δ_j of the interacting beads from $\chi_{ij} = \frac{V_{\text{ref}}(\delta_i - \delta_j)^2}{k_B T}$ with V_{ref} as a reference average bead volume. This reference volume is taken equal to the average bead volume $\sim 1.19 \text{ nm}^3$. The solubility parameters of PET and PA56 were determined by the group contribution method to be 19.29 and 22.62 $(\text{J}/\text{cm}^3)^{1/2}$, respectively.^[42,43] As a result, the maximum repulsion coefficients between PA56/PET pairs were calculated and are given in **Table 1**. In this work, the friction coefficient ξ_{ij} was set to $4.5 (mk_B T / r_c^2)^{1/2}$ between all bead types. Finally, the fluctuation-dissipation theory was used to define the noise amplitude σ_{ij} as $\sigma_{ij}^2 = 2\xi_{ij}k_B T$. In all systems, the force cutoff radius was set to $2 r_c$.

Table 1. The maximum repulsion coefficients of different pairs used in DPD simulations.

Pair type	PET	PA56
PET	25.00	30.75
PA56	30.75	25.00

The simulations were performed in an orthogonal cubic box with a side of $22 r_c$ which corresponds to 33.66 nm in real units. Periodic boundary conditions were applied on all sides of the box. A bead number density of 3 was achieved in the simulations by dispersing a total of 32000 beads of different types in the box. The simulated systems contain different volume fractions of PA56 which are equivalent to 10, 15, 20 and 30 wt% of PA56 beads in the final blends - the same as the experimental samples. The simulations were carried out in the NVT ensemble. The systems were constructed with a random dispersion of chains within the box. This configuration was allowed to equilibrate for 10×10^6 steps to achieve the fully-

equilibrated morphology of the blends. The time step was set to 0.01τ in all simulations. Therefore, the equilibration runs correspond to a real time of $2.2 \mu\text{s}$.

4. Results and Discussion

4.1. Microstructure of PA56/PET Blends

In order to highlight the microstructure of PA56/PET blends, etching with formic acid was applied to dissolve the PA56 phase by exposing the surface of the cryofractured specimens. **Figure 2** depicts scanning electron microscope (SEM) micrographs of the prepared blends as well as the untreated specimens. The fractured samples show clearly that PET constitutes the continuous phase of the blend, and PA56 is the dispersed phase. The dispersed PA56 domains are randomly distributed in PET forming the so-called sea-island morphology. After etching of the PA56 phase, a smooth and distinct interface is observed between the polymers suggesting an incompatible mixing. Similar morphological patterns have been previously observed in PET blends containing commercial PA6 and PA66.^[27–30] In particular, the poorly compatible PET and PAs are used in the development of *in-situ* microfibrillar composites with enhanced directional properties.^[20,26,44,45] For the production of segmented pie fibers, this notion hints the possibility of an easy mechanical separation without the need for a solvent recycling side process during the processing.

Figure 2. SEM pictures of PA56/PET blends with different PA56 contents before and after etching with formic acid. The amount of PA56 in PA56/PET blends are (a) 0% (neat PET), (b) 100% (neat PA56), (c1 to c3) 10%, (d1 to d3) 15%, (e1 to e3) 20%, and (f1 to f3) 30%. The untreated samples are shown in parts a, b, c1, d1, e1, and f1. The samples shown in parts c2, d2, e2, and f2 were etched for 48 hours and c3, d3, e3, and f3 for 96 hours, respectively.

In **Figure 3** TEM microstructure images of PA56/PET blends are shown. The pictures confirm an ellipsoidal shape of dispersed PA56 phase in PET matrix. These ellipsoidal structures can be attributed to shear and elongation stresses exerted during the mixing. An equivalent circular droplet radius was estimated for the ellipsoidal shapes to provide a

measure of the dispersed phase size. At the lowest content of PA56 in PET, the dispersed phase average size is 1.5 μm . With increasing PA56 content, the average size gradually increases up to 3.5 μm , and the interface between the two phases becomes more apparent to distinguish. This observation suggests that the PA56 content affects the compatibility of the blend to some extent with minor partial immiscibility taking place at lower PA56 contents. This behavior could be a result of partial chain inter-diffusions of the polymers at a molecular level. However, the overall microstructure of the blends suggests immiscibility with a poor blending compatibility.

Figure 3. TEM images of PA56/PET blends with PA56 contents of (a) 10%, (b) 15%, (c) 20%, and (d) 30%.

Phase separation and formation of dispersed droplets within the matrix start at a molecular level. This length scale, however, is hardly accessible by experiments. In order to investigate the compatibility of PET and PA56 on the molecular level, we employed the DPD technique which has proven to be a powerful tool to predict the phase behavior in polymeric materials. The equilibrium morphologies of blends corresponding to the experimental samples (**Figure 3**), were simulated and are shown in **Figure 4**. With these simulations, it is possible to follow

how the phase separation patterns develop at the molecular level in the molten state before the samples undergo any crystallization. One should note that a random dispersion of PA56 and PET molecules was used as the starting morphology for the simulations. Therefore, the equilibrium morphologies are purely thermodynamically driven rather than being a consequence of topological constraints. Due to such an initial morphology, the probability that the PA56 chains form a bundle is smaller for lower PA56 contents. This is clearly realized for the simulations with the lowest amount of PA56 (**Figure 4a**) where partial blend immiscibility is predicted on a molecular level. However, the dispersed phase forms larger bundles which can eventually result in a co-continuous morphology by increasing the PA56 content, see **Figure 4d**. These observations are in agreement with the trends in our microscopy data and can help interpret the following crystallization mechanism during the cooling of the samples. Considering the relation between the temperature and the maximum repulsion coefficients through the Flory-Huggins parameter,^[32] one can expect that the PA56 and PET chains become even more repellant to one another, thereby intensifying the phase separation during the cooling. Therefore, the simulated blend morphologies can become increasingly coarsened, i.e. phase separated, upon decreasing the temperature. Still, one should note that our current simulations are not comprehensive enough to make decisive conclusions on this matter. In order to discover how the crystallization phenomena might promote and/or diminish the phase separation at lower temperatures a further study would be required.

Figure 4. The equilibrium morphology of PA56/PET blends with various wt/wt ratios of (a) 90/10, (b) 85/15, (c) 80/20, and (d) 70/30 at the end of the microscopic DPD simulation runs. PA56 and PET beads are shown in red and turquoise, respectively.

The incompatibility and dispersed morphology formation of the bio-based PA56 in PET should also manifest itself during the mixing. For this reason, the blending process was monitored by measuring the torque during the kneading, see **Figure 5a**. One can observe that torques of all blended PA56/PET compositions initially increased up to a sharp peak, and then decreased rapidly with time until a steady state was reached. The final torques vs composition in PA56/PET blends are also illustrated in **Figure 5a** as the inset. The steady-state torques of the blends are lower than those of neat PET, and they increase when the PA56 content is increased. The results demonstrate that a minimal torque is reached with a PA56 content of 10% in PA56/PET blends. It is possible that minor addition of PA56 could act as a lubricant in PET by reducing the internal friction of PET chains. This mobility enhancement of polymer

molecules may then result in a reduced torque, which is lowest with 10% of PA56. With further increase of PA56 content, the final torque increases, which can be explained by the formation of relatively larger domains of the dispersed PA56 phase within PET. In order to check the influence of the PA56 content on its molecular mobility within the blends, we calculated the average mean-squared-displacements (MSD) of the PA56 particles in the DPD simulations according to $MSD = \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle$ with $\mathbf{r}_i(t)$ and $\mathbf{r}_i(0)$ representing the position vectors of the i th particle at the start of the simulation and at time t , respectively.^[46] The MSD profiles show that the overall movements of the PA56 particles cover larger distances as the dispersed phase content increases, see **Figure 5b**. This observation is expected since the unfavorable repulsive PET medium is less restricting against the movements of PA56 particles as they grow in size and occupy a larger volume in the box. Therefore, one can deduce that the larger domains of PA56 and not the molecular mobility of the dispersed phase are responsible for the increasing torque with PA56 content. As the PA56 content is increased, higher stresses are necessary in order to break apart and move the dispersed phase in PET matrix against the strong driving forces which promote the phase separation. A statistical analysis of PA56 droplet size distribution in the PA56/PET blends based on residual hole size after 96h etching of the dispersed phase supports the hypothesis of the increased dispersed domain size, see **Figure S 2** of the Supporting Information. The graphs show that the mean particle size of the PA56 dispersed in PET increases with increasing PA56 content.

Figure 5. (a) Mixing torque of PET, PA56 and PA56/PET blends with different PA56 contents. The inset of the plot shows the steady state mixing torque vs. the amount of PA56 in the blends. (b) The average mean-squared-displacements (MSD) of the PA56 particles in the DPD simulations for different PA56/PET blends.

4.2. Crystallization Behavior

Crystallization behavior and spherulite growth of semi-crystalline polymers is visualized by using hot stage POM as depicted in **Figure 6**. **Figure 6a** and **b** clearly show that neat PET and PA56 are readily crystallizing polymers, with PA56 having larger spherulites than PET. The addition of PA56 to PET, however, considerably changes the respective crystallization behavior. The developed crystals during the cooling step in the hot stage POM (**Figure 6c** to **f**) are significantly smaller than the ones of the neat polymers. Therefore, by adding PA56 to PET, only small crystals can develop in the blend. To clarify how PA56 influences the crystallization processes, the crystallization sequence of the two components in the blend was studied by utilizing the DSC heating and cooling curves. While POM provides local information about the shape and size of the crystals on the micrometer length scale, DSC offers insight for the overall behavior of the blends at a larger length scale. Consequently, these data can be complementary to each other in a multiscale framework. It should be noted that PET and PAs are often sensitive to the processing protocols and can undergo various molecular reformations (e.g. change of molecular weight and structure) during their

processing. Such changes can influence the crystallization behavior significantly. Despite the importance of such molecular alterations, a proper characterization of their correlations cannot be easily established. For instance, a variety of chemical reactions are known in the literature to occur in PET during its high-temperature melt processing which strongly depend on the processing temperature, the ambient humidity, and the initial structure of the polymer itself.^[17,47–49] Considering the complexity of such phenomena and the main purpose of this paper, a further study is necessary to comment on the role of such molecular changes on the crystallization behavior of the blends.

Figure 6. POM images of the pure polymers and PA56/PET blends with PA56 contents of (a) 0% (neat PET), (b) 100% (neat PA56), (c) 10%, (d) 15%, (e) 20%, and (f) 30%.

In the DSC curves of the blends in the second heating step, two melting peaks (T_{M1} , T_{M2}) can be distinguished (**Figure 7a**), with T_{M1} being higher than the melting temperature of both neat PA56 and PET, and T_{M2} being lower (**Table 2**). As the peak height of T_{M1} decreases with increasing PA56 content, and that of T_{M2} increases, T_{M2} can be attributed to the PA56 melting peak. Therefore, the melting temperature of the PA56 phase in the PA56/PET blends is considerably lower than the melting temperature of the neat PA56 polymer. This could be the effect of a modified crystallization of PA56 by the presence of the PET phase during the crystallization. This becomes more apparent after considering the DSC cooling curves. The DSC cooling curves of the PA56/PET blends are shown in **Figure 7b**. The occurrence of two independent crystallization peaks in the blends which are different than those of the neat polymers shows that PA56 and PET influence each other's crystallization. When going from lower to higher PA56 content, the area of the crystallization peak with the lower temperature is increasing, while the area of the other crystallization peak is decreasing. Hence, the higher crystallization temperature in the blend can be attributed to PET and the lower to PA56. The attribution of the crystallization temperatures of the neat polymers, however, is opposite to the one observed in the blends. Hence, it can be concluded that PA56 is the first component which starts to form crystal nuclei during the cooling step (considering the higher T_C of the neat PA56 being higher than the one of the neat PET). Yet, further growth of these nuclei is hindered by the initiation of the PET crystallization before they can evolve into larger PA56 crystals. At this stage, the PA56 nuclei can act as a nucleating agent for PET, thereby accelerating the nucleation rate of PET and shifting its crystallization temperature peak to higher values (**Table 3**). The emerging crystallization enthalpy of the PET locally hinders the material to follow the external temperature program thus obstructing the growth of the PA56 nuclei to crystals. As the amount of PA56 is increased in the blend, the number of PA56 nuclei also becomes larger. Hence, a smaller PA56 content will result in a smaller number of

relatively large PET crystals, while a larger number of PA56 nuclei in blends with a higher PA56 content will result in numerous small crystals. This behavior is also witnessed in the POM results in **Figure 6**. It is noteworthy that the absence of any emerging additional crystallization peaks other than those ascribed to the PET and PA56 crystals hints that no co-crystallization of the two polymers takes place in the blends. We further confirm this hypothesis by XRD (cf. below). In non-isothermal crystallization kinetics, the shape of the high- and low-temperature sides of the crystallization peak in DSC is controlled by the nucleation and the crystal growth rates, respectively.^[30] The high-temperature side of the PET crystallization peak is narrowed in its blends compared to its neat state while its low-temperature-side is almost unchanged. This observation supports the hypothesis that the nucleation rate in PET is increased in its blends with PA56 while its crystal growth is not influenced significantly. The PA56 peak is, however, slightly broader on both sides in the blends suggesting a slowed-down nucleation and crystal growth kinetics. Similarly, a decrease in the non-isothermal crystallization kinetics was observed for PA6 in PA6/PET blends.^[30]

Figure 7. DSC curves for (a) second heating and (b) cooling of PA56/PET blends with different PA56 contents. Half-time of crystallization $t_{1/2}$ during non-isothermal crystallization of PET (c) and PA56 (d) in PA56/PET blends, as a function of the cooling rate ϕ .

Table 2. DSC data for second heating of PA56/PET blends with different PA56 contents.

PA56 (%)	content	Second heating cycle		
		$T_{M1,peak}$ (°C) (PET)	$T_{M2,peak}$ (°C) (PA56)	$\Delta H_{m,total}$ (J/g)
0 (PET)		253.9	-	34.1
10		255.3	247.5	45.2
15		255.6	247.9	46.4
20		255.7	247.7	49.4
30		256.1	247.9	53.4
100 (PA56)		-	254.6	56.3

Table 3. DSC data for cooling of PA56/PET blends with different PA56 contents. T_{Ci} ($i = 1,2$) represent the crystallization temperatures of the PET and PA56 components, respectively. Enthalpy values $\Delta H_{Ci \text{ bl}}$ ($i = 1,2$) are reported related to the entire mass of the sample (J/g sample), while enthalpy values $\Delta H_{C1 \text{ PET}}$ and $\Delta H_{C2 \text{ PA56}}$ are given related to the individual components only. The latter were calculated by multiplying the former with the weight fraction of the respective component in the blend.

PA56 content (%)	T_{C1} (°C) (PET)	$\Delta H_{C1 \text{ bl}}$ (J/g sample) (PET)	$\Delta H_{C1 \text{ PET}}$ (J/g PET) (PET)	T_{C2} (°C) (PA56)	$\Delta H_{C2 \text{ bl}}$ (J/g sample) (PA56)	$\Delta H_{C2 \text{ PA56}}$ (J/g PA56) (PA56)	$\Delta T_i = T_{Mi} - T_{Ci}$	
							ΔT_1 (°C) (PET)	ΔT_2 (°C) (PA56)
0 (PET)	189.1	41.9	41.9	-	-	-	64.8	-
10	204.1	41.6	46.2	157.4	3.6	36.0	51.2	90.1
15	204.2	38.5	45.3	160.2	6.3	42.0	51.4	87.7
20	204.7	33.5	41.9	163.7	9.9	49.5	51.0	84.0
30	205.2	30.4	43.4	169.3	17.8	59.3	50.9	78.6
100 (PA56)	-	-	-	201.7	59.3	59.3	-	52.9

According to the data in **Table 2**, the melting points of the PET crystals in the blends are slightly higher than the melting point of the neat polymer. This can be ascribed either to properties of the PET crystals (e.g. size, quality, shape) in the blend or to a retardation effect by the (endothermic) melting process of the PA56 crystals which is still in progress when the PET crystals start to melt. Since the PET crystals in the blends are considerably smaller than in the neat polymer, the second explanation is considered to be the main reason for the observed increase in the melting point. Further investigation of the DSC data as shown in **Table 3** reveals that for the blend with 10% PA56, the crystallization enthalpy $\Delta H_{C1 \text{ PET}}$ of PET is approx. 10% higher than the value for the neat polymer. This notion is another indication of the promotion of PET crystallization by PA56 as described before. With higher

PA56 contents in the blend, however, this promotion effect is smaller and the PA56 crystallization (suppressed in blends with a low PA56 content) gains momentum. This behavior is also manifested in the increasing $\Delta H_{C2 \text{ PA56}}$ values. Another indication for the general promotion of PET crystallization in the blends are the subcooling values $\Delta T_i = T_{Mi} - T_{Ci}$ reported in **Table 3**. The ΔT_i values are lower for PET in blends than for the neat PET polymer, while they are heavily increased for the PA56 component in the blend compared with the neat PA56. However, the fact that the ΔT_2 values for PA56 are decreasing when going to higher PA56 contents in the blend confirms that this promotion effect becomes more marginal by increasing the PA56 content. Finally, the overall promotion effect of PET crystallization by PA56 addition becomes evident by examining the half-time of crystallization $t_{1/2}$ as a function of the cooling rate (**Figure 7c,d**). In general, a higher cooling rate leads to smaller $t_{1/2}$ values. The addition of PA56 to PET, however, remarkably shortens $t_{1/2}$ for PET, especially at slow cooling rates (**Figure 7c**). On the other hand, $t_{1/2}$ of PA56 shows the opposite tendency (**Figure 7d**). Therefore, the DSC analyses show that with PA56 acting as a nucleating agent, the minor phase accelerates the crystallization rate of the matrix.^[50]

As the POM and DCS tests reveal altered crystallization processes of PET and PA56 in the blends compared with the neat polymers, one might expect differences in the crystal forms and chains packing on a molecular level. In order to explore possible crystal reformations in the blends as compared with the neat polymers, we performed XRD measurements on the samples. **Figure 8a** shows the XRD patterns (2θ scan) of neat PET and neat PA56. For the neat PA56, a strong peak at 21.6° dominates the pattern. According to Puiggalí et al.^[51] this peak indicates the presence of the crystalline γ -form of PA56 and can be assigned to its (100)/(110)/(010) planes. Additional peaks appearing at 12.8° and 37.5° can be assigned to the γ -form (004) and (210) planes, respectively. Two shoulder peaks at 20.9° and 23.6° ,

however, belong to the (020) and the (110) plane of the α -form of PA56.^[51] PA56 is known to show polymorphism, depending on the conditions of the sample preparation. In a closely related example, the role of drawing pressures on the XRD patterns is manifested in melt-spun bicomponent PA6/PET fibers by Wang et al.^[52] Coexistence of the α - and γ -forms has also been found by Magill^[53] in spherulites crystallized from the melt, whereas the α -form was predominant in fibers formed by rapidly withdrawing a glass rod from the melt and subsequent drawing above room temperature^[53] or in annealed fibers.^[51] Spherulitic films cast from formic acid solution even showed exclusively the α -form.^[53] The 2θ scan of the neat PET reveals peaks at 16.1° (0-11), 17.5° (0-10), 21.4° (1-1-1), 22.6° (1-10) and 26.0° (100) as expected from its crystal structure.^[54]

Figure 8. (a) XRD patterns (2θ scan) of neat PET, neat PA56 and the PA56/PET blend with 30% PA56 content. (b) XRD patterns of PA56/PET blends with different PA56 contents.

Figure 8b shows the evolution of the 2θ scans as a result of blending PET with PA56. In the blends, the peak of γ -PA56 at 21.6° , which is predominant in the XRD pattern of the neat PA56, does not appear. The PET-peak at 21.4° , however, seems to shift towards smaller 2θ values. Since a shift of only one of the PET peaks is quite unlikely, this “shift” can be interpreted as the result of the combination of this PET peak with the increasing peak of α -PA56 at 20.9° . The shoulder at 21.6° in the XRD pattern of the blend with 30% PA56 indicates that this blend still contains some γ -PA56 (also shown in **Figure 8a**). Hence, similar

to the neat PA56 phase, a coexistence of the α -form and the γ -form of PA56 can also be observed in its blends with PET. Still, the presence of the PET phase and the resultant changes in crystallization temperatures and the speed of the crystallization process, as described above, influence the relative amount of the α -form and the γ -form in the PA56 phase. Therefore, the packing of PA56 chains changes between α -form and γ -form due to different hydrogen bond directions when added to PET.^[51] Before closing this section, it should be noted that there is no emerging crystalline diffraction other than those of PET and PA56. This notion along with the DSC results suggest that the two polymers form separate crystals and do not undergo co-crystallization. Consequently, an enhancement in the mechanical properties of the blends as a result of the compatibilization via crystallite interpenetration at the interface (a mechanism suggested for PA66/PET blends by some authors^[55]) is very unlikely in PA56/PET samples. The weak interfacial adhesion (due to the poor physical interlocking of components at the interface during melt cooling) in PA56/PET in comparison with PA66/PET is an advantage for the fabrication of bicomponent segmented pie fibers. For PA6/PET blends, on the other hand, an interphase thickness of ~ 0.47 nm reported by Wang et al.^[29] suggests a similarly weak interfacial adhesion suitable for bicomponent splittable fibers as also witnessed in experimental products.^[52]

5. Conclusions

In this paper, the morphology and crystallization of PA56/PET blends with different contents of bio-based PA56 was investigated by utilizing a range of experimental as well as simulation techniques. The SEM and TEM images showed that the prepared blends are immiscible at all PA56 contents. DPD simulations of the under-equilibrium morphologies further confirmed these results on a molecular level indicating a partial miscibility at the lowest PA56 content to a complete phase separation for the highest content. Microscopy and simulation methods also

showed an increase in the dispersed domain size upon increasing PA56 content. The mixing torques of the kneader indicated that lower steady-state torques are required for the PA56/PET blends as opposed to the neat PET. The minimum value for the steady-state torque was for the lowest PA56 amount, i.e. 10%. It was verified that larger dispersed domains form by increasing the PA56 amount which makes it more difficult to disperse them in the thermodynamically undesired PET matrix. Overall, a lubricating effect was observed for PA56 in PET matrix due to the lower torque values which favors an easier processing of their blends. The crystallization behavior of PA56/PET blends was also analyzed by incorporating POM, DSC and XRD methods. With the addition of PA56 to PET, both polymers formed smaller crystals compared with their neat states. It was discussed that in a DSC cooling cycle the early formation of PA56 crystals promotes PET crystallization by acting as a nucleating agent. The exothermic crystallization of PET would then hinder further PA56 crystallization. Consequently, both polymers eventually form numerous small crystals compared with several large crystals in their neat samples. It was further discussed based on XRD patterns that the molecular packing of PA56 chains is changed in the blends.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author

6. References

- [1] *The Establishment of Modern Polymer Science By Wallace H. Carothers*, American Chemical Society, Delaware, **2000**.
- [2] C. K. Williams, M. A. Hillmyer, *Polym. Rev.* **2008**, 48, 1.
- [3] B. A. J. Noordover, In *Renewable Polymers* John Wiley & Sons, Inc., Hoboken, NJ, USA **2011**; pp. 305–354.

- [4] L. S. Severino, D. L. Auld, M. Baldanzi, M. J. D. Cândido, G. Chen, W. Crosby, D. Tan, X. He, P. Lakshmmamma, C. Lavanya, O. L. T. Machado, T. Mielke, M. Milani, T. D. Miller, J. B. Morris, S. A. Morse, A. A. Navas, D. J. Soares, V. Sofiatti, M. L. Wang, M. D. Zanotto, H. Zieler, *Agron. J.* **2012**, *104*, 853.
- [5] Y. Xia, R. C. Larock, *Green Chem.* **2010**, *12*, 1893.
- [6] NishiK., EndoS., MoriY., TotsukaK., HiraoY., *Publ. Appl. with search Rep. - Eur. Pat. Off.*, **2004**, PAT-EP14, 20 pp.
- [7] S. Kind, C. Wittmann, *Appl. Microbiol. Biotechnol.* **2011**, *91*, 1287.
- [8] M. Li, D. Li, Y. Huang, M. Liu, H. Wang, Q. Tang, F. Lu, *J. Ind. Microbiol. Biotechnol.* **2014**, *41*, 701.
- [9] L. Morales-Gámez, D. Soto, L. Franco, J. Puiggali, *Polymer* **2010**, *51*, 5788.
- [10] Y. A. Eltahir, H. A. M. Saeed, Y. Xia, H. Yong, W. Yimin, *J. Text. Inst.* **2016**, *107*, 208.
- [11] Y. A. Eltahir, H. A. M. Saeed, C. Yuejun, Y. Xia, W. Yimin, *Text. Res. J.* **2014**, *84*, 1700.
- [12] R. Hufenus, Y. Yan, M. Dauner, D. Yao, T. Kikutani, In *Handbook of Fibrous Materials Vol 1*, J. Hu, Ed.; Wiley-VCH Publishing Ltd. **2018**;
- [13] A. A. Leal, O. A. Neururer, A. Bian, A. Gooneie, P. Rupper, K. Masania, C. Dransfeld, R. Hufenus, *Polymer* **2018**, *142*, 375.
- [14] F. Intini, S. Kühtz, *Int. J. Life Cycle Assess.* **2011**, *16*, 306.
- [15] D. H. Kang, R. Auras, J. Singh, *Resour. Conserv. Recycl.* **2017**, *116*, 45.

- [16] K. K. Leonas, S. S. Muthu, Ed.; Springer, Singapore **2017**; pp. 55–77.
- [17] F. Awaja, D. Pavel, *Eur. Polym. J.* **2005**, *41*, 1453.
- [18] H. Khoshnevis, A. Zadhoush, *Rheol. Acta* **2012**, *51*, 467.
- [19] W. Wu, C. Wan, H. Zhang, Y. Zhang, *J. Appl. Polym. Sci.* **2014**, *131*, 40272.
- [20] M. Evstatiev, S. Fakirov, J. M. Schultz, K. Friedrich, *Polym. Eng. Sci.* **2001**, *41*, 192.
- [21] L. Z. Pillon, L. A. Utracki, *Polym. Eng. Sci.* **1984**, *24*, 1300.
- [22] C.-C. Huang, F.-C. Chang, *Polymer* **1997**, *38*, 4287.
- [23] J. John, M. Bhattacharya, *Polym. Int.* **2015**, *49*, 860.
- [24] K. Chiou, F. Chang, *J. Polym. Sci. Part B Polym. Phys.* **2000**, *38*, 23.
- [25] H. He, L. Chen, S. Sun, T. Wang, Y. Zhang, M. Zhu, *Fibers Polym.* **2014**, *15*, 744.
- [26] M. Evstatiev, N. Nicolov, S. Fakirov, *Polymer* **1996**, *37*, 4455.
- [27] C. K. Samios, N. K. Kalfoglou, *Polymer* **1999**, *40*, 4811.
- [28] I. Goitisoló, J. I. Eguiazábal, J. Nazabal, *Compos. Sci. Technol.* **2010**, *70*, 873.
- [29] J. Wang, D. Langhe, M. Ponting, G. E. Wnek, L. T. J. Korley, E. Baer, *Polymer* **2014**, *55*, 673.
- [30] Y. Huang, Y. Liu, C. Zhao, *J. Appl. Polym. Sci.* **1998**, *69*, 1505.
- [31] Q. Zhang, Z. Zhang, H. Zhang, Z. Mo, *J. Polym. Sci. Part B Polym. Phys.* **2002**, *40*, 1784.
- [32] R. D. Groot, P. B. Warren, *J. Chem. Phys.* **1997**, *107*, 4423.

- [33] A. Gooneie, S. Schuschnigg, C. Holzer, *Polym.* **2017**, 9, 16.
- [34] M. P. Fernández-Ronco, B. Gradzik, A. Gooneie, R. Hufenus, M. El Fray, *ACS Sustain. Chem. Eng.* **2017**, 5, 11060.
- [35] A. Gooneie, R. Hufenus, *Macromolecules* **2018**, acs. macromol.8b00585.
- [36] J. Sapkota, A. Gooneie, A. Shirole, J. C. Martinez Garcia, *J. Appl. Polym. Sci.* **2017**, 134, 45279.
- [37] A. Gooneie, J. Gonzalez-Gutierrez, C. Holzer, *Polym.* **2016**, 8, 361.
- [38] A. Gooneie, C. Holzer, *Polymer* **2017**, 125, 90.
- [39] A. Gooneie, J. Sapkota, A. Shirole, C. Holzer, *Polymer* **2017**, 118, 236.
- [40] Y. A. Eltahir, H. A. M. Saeed, Y. M. Xia, Y. M. Wang, *Adv. Mater. Res.* **2014**, 937, 86.
- [41] J. Brandrup, E. H. Immergut, E. A. Grulke, *Polymer Handbook*, Wiley-Interscience Publication, 4th edn., **2003**.
- [42] D. Karst, Y. Yang, *J. Appl. Polym. Sci.* **2005**, 96, 416.
- [43] R. F. Fedors, *Polym. Eng. Sci.* **1974**, 14, 147.
- [44] M. Evstatiev, S. Fakirov, G. Bechtold, K. Friedrich, *Adv. Polym. Technol.* **2000**, 19, 249.
- [45] S. Fakirov, *Compos. Sci. Technol.* **2013**, 89, 211.
- [46] A. Gooneie, S. Schuschnigg, C. Holzer, *Macromol. Theory Simulations* **2016**, 25, 287.
- [47] L. K. Nait-Ali, X. Colin, A. Bergeret, *Polym. Degrad. Stab.* **2011**, 96, 236.
- [48] R. Assadi, X. Colin, J. Verdu, *Polymer* **2004**, 45, 4403.

- [49] M. Kruse, M. H. Wagner, *Rheol. Acta* **2016**, *55*, 789.
- [50] S. P. Jape, V. D. Deshpande, *Thermochim. Acta* **2017**, *655*, 1.
- [51] J. Puiggalí, L. Franco, C. Alemán, J. A. Subirana, *Macromolecules* **1998**, *31*, 8540.
- [52] M. Wang, B. Yu, J. Han, W. Song, F. Zhu, *J. Ind. Text.* **2017**, *46*, 1281.
- [53] J. H. Magill, *J. Polym. Sci. Part A Gen. Pap.* **1965**, *3*, 1195.
- [54] C. W. Bunn, R. de P. Daubeny, C. W. Bunn, *Proc. R. Soc. London* **1954**, *226*, 531.
- [55] L. A. Utracki, B. D. Favis, In *Handbook of Polymer Science and Technology, Volume 4*, N. P. Cheremisinoff, Ed.; Hanser Publishers, Munich **1989**; p. 128.