

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



---

# Cellulose Acetate for Thermoplastic Foam Extrusion

---

Stefan Zepnik, Tilo Hildebrand, Stephan Kabasci,  
Hans-Joachim Ra-dusch and Thomas Wodke

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/56215>

---

## 1. Introduction

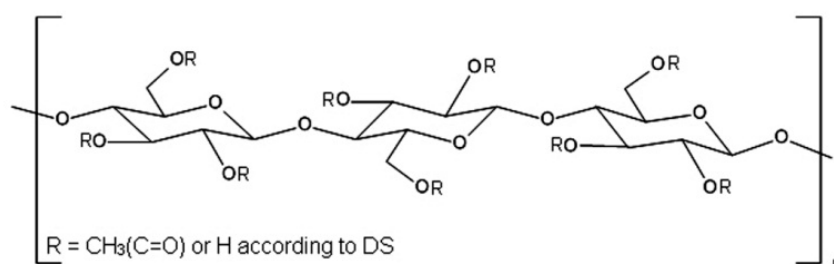
Foam extrusion is a well established and widely used process to produce foamed products for packaging, construction, insulation or technical applications. Generally, extruded foams are produced by generating small gas bubbles in the polymer melt. These gas bubbles can be created either by means of chemical blowing agents (CBA) or physical blowing agents (PBA). The blowing agent is the primary factor which controls the foam density [1]. Along with the foam morphology this determines the end-use properties of the foam. In the case of chemical foaming the CBA, often as masterbatch or powder, is fed into the extruder together with the polymer. Due to heat dissipation during melt processing, the CBA decomposes or reacts either endothermically or exothermically and produces foaming gases such as water, carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>) or nitrogen (N<sub>2</sub>). The resulting foam density is usually limited to 400-800 kg m<sup>-3</sup> as CBAs are too expensive to make foams below 400 kg m<sup>-3</sup> [1]. As a consequence, physical blowing agents (PBA) are used for low density foams. Basically, low boiling liquids such as water or gases like CO<sub>2</sub> or butane are used. The feeding process, the mixing of the polymer with the PBA as well as the control of the overall foaming process is more difficult for physical foaming. Specific machineries and knowledge about the complex physical foam extrusion process is often obligatory [2]. Understanding the relationship between the processing parameters and the polymer properties is fundamental to produce high quality foams [3]. For excellent foam extrusion behavior the polymer must fulfill specific thermal and rheological properties. Lots of research has been undertaken to investigate the melt rheology of conventional oil-based polymers with respect to their foamability [4-6]. Multi-axial stretching of the cell walls occurs during cell growth [5, 7]. As a consequence, adequate melt strength and melt extensibility are required. For effective dissolution of the blowing agent and for efficient mixing of the blowing agent with

the polymer melt a specific pressure inside of the extruder is required. Therefore, a certain minimum melt viscosity is also necessary. If the melt viscosity is too high partial solidification of the melt during foaming can lead to insufficient foam expansion, heterogeneous foam morphologies and poor foam properties [6, 8].

It is well known that melt rheology is closely linked to the chemical structure, the molecular weight, and the polydispersity (PD) or the molecular weight distribution (MWD) of the polymer [5]. A broad MWD or high PD, the incorporation of side chains or branched structures as well as blending linear with branched or cross-linked polymers are favorable for good foam extrusion behavior. Blends of linear and branched polypropylene (PP), cross-linked polyethylene (PE) or blends of low-density polyethylene (LDPE) and high-density polyethylene (HDPE) are good examples for improved melt strength, melt extensibility, and consequently good foaming behavior [4, 9-13]. Chain extension of recycled poly(ethylene terephthalate) (PET) significantly improves the rheological properties and foaming behavior [14]. Blends of polystyrene (PS) with different molecular weights lead to bimodal MWD. These blends exhibit improved strain hardening and melt strength [15]. As melt rheology is strongly temperature-dependent, the thermal and thermoplastic properties of the polymer are important parameters to control nucleation and cell growth and to stabilize the overall foam network. The melt processing range and the corresponding window of foamability largely depend on the type of polymer used [3]. Basically, semi-crystalline polymers have smaller processing ranges than amorphous polymers due to specific windows of melting and crystallization. Biopolymers are typically sensitive to thermo-mechanical stress during processing. They often exhibit a small processing range and significant loss of their physical properties due to thermal degradation at high temperatures, strong shearing or long residence time in the molten state. A broad processing range without thermal degradation is needed to adjust the required melt properties of biopolymers for good foam extrusion. Therefore, the improvement of rheological properties as well as the broadening of the thermoplastic processing window is essential to increase the application of biopolymers for foamed products. In foam extrusion, the blowing agents used have an enormous effect on the thermal and rheological properties [4, 5, 16-18]. A dissolved blowing agent in the polymer melt can act as plasticizer. The addition of a blowing agent generally reduces the melt viscosity and the glass transition temperature of the polymer. However, the plasticizing effect largely depends on the type of blowing agent (physical or chemical), the concentration used, and the mutual behavior (solubility, diffusivity) of the blowing agent with the polymer melt. Hence, knowledge about the thermal and the rheological properties of polymer/blowing agent mixtures is as important as the properties of the polymer itself.

Today, polyethylene (PE), polypropylene (PP), and polystyrene (PS) are the standard polymers used for foam extrusion. These conventional polymers are derived from petrochemicals and are not bio-based. Nowadays, the reduction of waste including greenhouse gas emissions as well as minimizing material use and energy efficiency are key factors for establishing sustainable products. Due to non-renewable resources, conventional oil-based polymers used for foam extrusion do not fulfill all of these requirements. Therefore, much effort is being made to replace petrochemical-based polymeric foams by

foams which are based on renewable resources such as starch or poly(lactic acid) (PLA) [19-26]. These biopolymers have several drawbacks especially if used for technical foamed products such as heat insulation. The low heat distortion resistance of PLA and the high moisture sensitivity of starch are the main disadvantages against using them as technical foams. Cellulose-based polymers are another promising group of biopolymers, which can be produced from a variety of raw materials, for example cotton, wood, and recycled paper. Organic cellulose esters such as cellulose acetate (CA), cellulose acetate butyrate (CAB), and cellulose acetate propionate (CAP) are bio-based polymers. They are produced through reaction of cellulose with organic acids, anhydrides or acid chlorides. Cellulose acetate is one of the oldest bio-based polymers in the world. It was first investigated by *Schützenberger* [27] in 1865. CA is produced in a two-step esterification process. At first, cellulose is activated and fully acetylated to cellulose triacetate (CTA). In a second step, a specific amount of water is added to CTA and the induced partial hydrolysis leads to partially substituted cellulose acetate [28, 29]. Cellulose acetates with a degree of substitution (DS) between 2.0 to 2.7 are usually used for thermoplastics [29]. The specific gravity of CA is about  $1.30 \text{ g cm}^{-3}$  and the refractive index is 1.48 [28]. In Figure 1, the general structure of cellulose acetate is shown.



**Figure 1.** General conformation of cellulose acetate.

CTA is well known for its polymorphism as it can crystallize in two-types of crystalline structures CTA I and CTA II [30]. Non-plasticized raw CA with a DS ranging from 1.75 to 2.7 shows also partially crystalline structures [30]. The crystallinity of these partially substituted CA is significantly lower due to less perfect and smaller crystallites [30]. External plasticization of partially substituted CA results usually in amorphous thermoplastic compounds [31] with high transparency and excellent optical properties. The thermal and mechanical properties are comparable to those of PS, styrene acrylonitrile copolymers (SAN) or poly(methyl methacrylate) (PMMA). Due to its properties, thermoplastic CA is a promising biopolymer for replacing PS in certain foam applications. Comparable to PS, the amorphous nature of plasticized CA is advantageous for foam extrusion applications due to the wider processing range accessible for foaming. However, pure CA exhibits strong interactions between its free hydroxyl groups (OH-groups) and has therefore a high glass transition temperature which is close to its thermal decomposition. As a result, unmodified CA cannot be processed using conventional thermoplastic processing technologies such as extrusion, injection molding or foaming. For melt processing, CA must be modified by means of blending or by external or internal plasticization. Blending of CA is difficult due to the high polarity and the strong intermolecular hydrogen bonds between the

free OH-groups [29]. Even CA/CAB blends or CA/CAP blends are immiscible despite their similar chemical structures [29]. Furthermore, foam extrusion of blends is more complex and more difficult as compared to homopolymers due to different melt flow behavior of the blend polymers and the selective solubility behavior of the blowing agent in the blend polymers. As a result, external plasticization by means of low molecular weight plasticizers is state of the art for melt processing of CA [29]. Research activities in the field of thermoplastic CA were limited over the last decades due to the focus on petrochemical-based polymers or other bio-based polymers such as PLA [29]. Nowadays, thermoplastic CA is no more than a niche product despite its good properties. Thus, data is scarce relating to the foamability and foam extrusion behavior of thermoplastic CA [32-34]. The existing patents [35-37] primarily describe foaming processes either for open-cell foams or for foamed filter rods. No systematic research has been published concerning the usability of CA for thermoplastic foam technologies such as foam extrusion. The relationship between the properties of externally plasticized CA, its foam extrusion behavior, and the final foam properties has not been studied in detail yet. The aim of this chapter is to discuss the suitability of externally plasticized CA for foam extrusion. The influence of external plasticization on thermoplasticity, thermal and rheological properties of CA is presented with respect to foam extrusion requirements. The flow behavior of an externally plasticized CA melt loaded with a blowing agent was also studied. Finally, preliminary foam extrusion tests were carried out and the general foam extrusion behavior of externally plasticized CA is presented. For these investigations, raw CA was obtained from Acetati SpA (Italy) as white powder with a DS of 2.5 and a molecular weight  $M_n$  around 50 000 g mol<sup>-1</sup>. Table 1 shows the non-toxic, bio-based, and biodegradable plasticizers used for external plasticization. Three different plasticizer concentrations – 15, 20, and 25 weight percentages (wt.-%) – were selected.

Plasticizer (Abbr.)	Formula	Molar mass [g mol <sup>-1</sup> ]	Molar volume [cm <sup>3</sup> mol <sup>-1</sup> ]	Boiling point (760 mmHg) [°C]
Allyl alcohol ethoxylate (AAE)	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	102.13	98.20	no data
Glycerol diacetate (GDA)	C <sub>7</sub> H <sub>12</sub> O <sub>5</sub>	176.17	149.30	245-280
Glycerol triacetate (GTA)	C <sub>9</sub> H <sub>14</sub> O <sub>6</sub>	218.21	187.95	250-270
Ethylene glycol diacetate (EGDA)	C <sub>6</sub> H <sub>10</sub> O <sub>4</sub>	146.14	130.48	180-190
Triethyl citrate (TEC)	C <sub>12</sub> H <sub>20</sub> O <sub>7</sub>	276.28	242.27	290-300
Acetyl triethyl citrate (ATEC)	C <sub>14</sub> H <sub>22</sub> O <sub>8</sub>	318.32	273.71	320-330

**Table 1.** Plasticizers used for external plasticization of CA and their corresponding properties.

## 2. Thermoplasticity and thermal properties

### 2.1. Influence of plasticizer on melt processing window

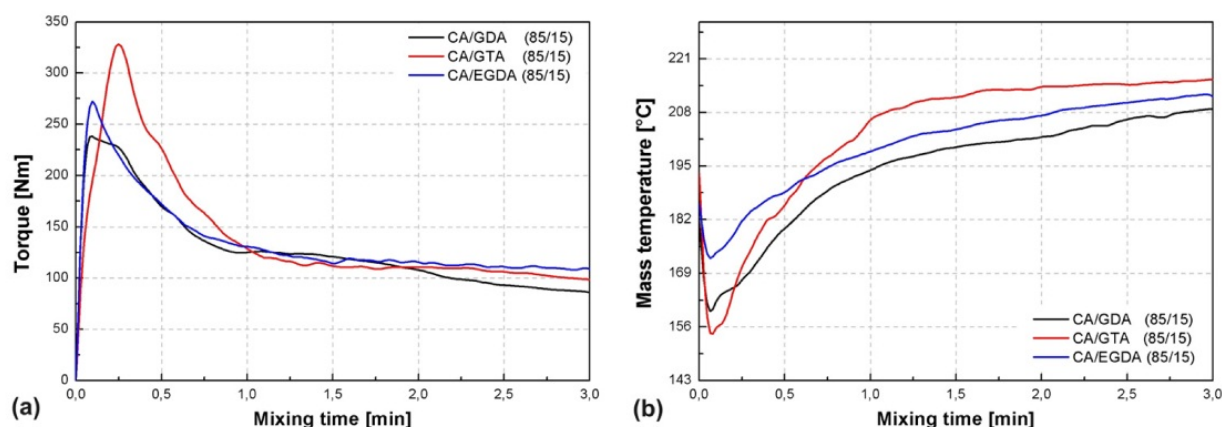
Melt processing performance of externally plasticized CA was investigated using an internal laboratory mixer with a chamber volume of around 370 cm<sup>3</sup> (Mixer W/N/B/S 350 Plasti-Corder® Lab-Station, Brabender). The processing temperature was set at 180 °C and the



rotational speed of the blades was kept constant at  $60 \text{ min}^{-1}$ . To minimize thermo-mechanical induced degradation of this biopolymer, mixing time was fixed at 3 min. The CA obtained from Acetati SpA (Italy) was premixed with the selected plasticizer at room temperature in a powder mixer. The dry blends were fed into the preheated chamber of the internal mixer. Mass temperature and torque were measured during melt processing. The specific mechanical energy input ( $SME$ ) in  $\text{J g}^{-1}$  was calculated from the torque-time graphs according to Eq. (1) [38]

$$SME = \frac{\omega}{m} \cdot \int_0^{t_{\max}} C(t) dt \quad (1)$$

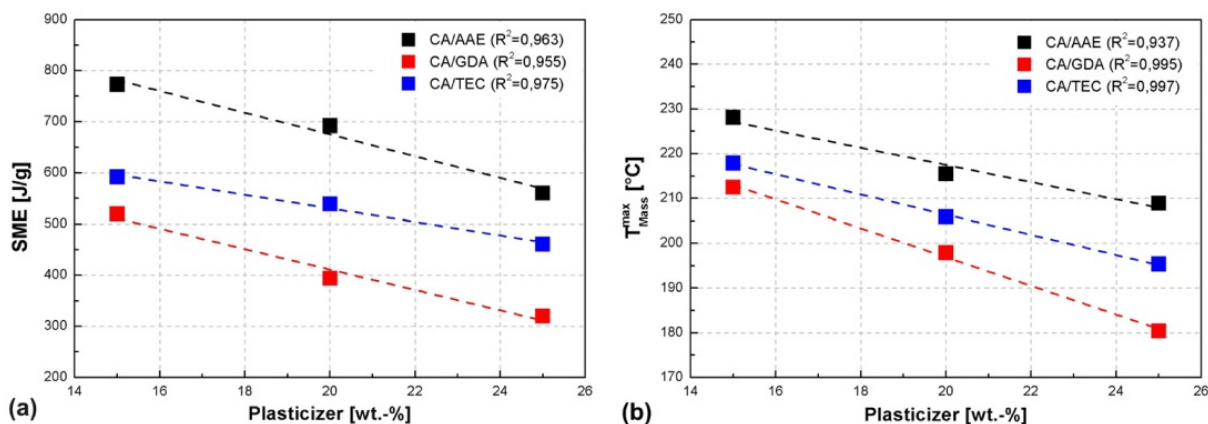
where  $\omega$  is the rotor speed,  $m$  is the sample mass,  $C(t)$  is the torque at time  $t$  and  $t_{\max}$  is the mixing time. For melt processing of highly substituted CA, an appropriate amount of plasticizer is necessary due to the extremely narrow window between melting and thermal degradation of pure CA [31]. Figure 2 shows typical kneader graphs as a function of mixing time in dependence of plasticizer type using equal plasticizer contents.



**Figure 2.** (a) Torque and (b) mass temperature of externally plasticized CA compounds as a function of mixing time and plasticizer type at constant plasticizer content (15 wt.-%).

When using a highly miscible plasticizer, improved melt processing of CA is achieved. This is expressed by lower torque and mass temperature during mixing. Highly miscible plasticizers can strongly decrease the intra- and intermolecular forces. Thus, higher chain mobility and lubricity is achieved. Consequently, lower torque for melting and mixing is required. This is very important for stable melt processing of CA as lower torque input means less shearing. Heat dissipation and overall thermo-mechanical stress are lower, and thus degradation of CA during mixing is minimized. Similar results can be achieved by increasing the plasticizer content of a less miscible plasticizer due to increasing plasticizer fraction in the CA matrix, which causes stronger lubricity [32, 39]. As seen in Figure 3, the calculated  $SME$  and the maximum mass temperature during melt processing confirm the assumption above. An increase in plasticizer content leads to less shear (lower  $SME$ ) and less heat dissipation (lower mass temperature) during melt processing. As a conclusion, the more the plasticizer is compatible with CA, the better the plasticizing performance and the

broader the window for melt processing of CA becomes. However, it is not possible to add any amount of plasticizer due to saturation effects and solubility limits in the biopolymer matrix.



**Figure 3.** (a) SME input and (b) maximum mass temperature of selected externally plasticized CA compounds as a function of plasticizer type and content.

The obtained results for melt processing of externally plasticized CA are very important with respect to foam extrusion processes. The broader the window of melt processing of CA is, the easier it will be to adjust the rheology to the foam extrusion process and the wider the processing range for the foam extrusion process. The use of highly miscible plasticizers is favored as less amount of plasticizer is needed to achieve the desired properties. Less plasticizer evaporation during foam extrusion and less plasticizer migration during foam use may also occur when using a highly compatible plasticizer instead of a less miscible one.

## 2.2. Influence of plasticizer on thermal properties

As mentioned in the introduction, a broad melt processing range without thermal degradation of the biopolymer is necessary to adjust the required melt rheology for foam extrusion. Therefore, thermal stability of externally plasticized CA was studied using thermogravimetric analysis (TGA). A first run with a heating rate of 10 K min<sup>-1</sup> from 25 °C to 400 °C in nitrogen atmosphere was conducted to obtain general information on the thermal degradation behavior of externally plasticized CA. A second run with a heating rate of 10 K min<sup>-1</sup> from 25 °C to 400 °C in nitrogen atmosphere with an isotherm of 6 min at the boiling temperature range of the plasticizer was performed to get more information about plasticizer loss. The onset degradation temperature ( $T_{d^{onset}}$ ) was determined according to DIN EN ISO 11358. Table 2 summarizes the obtained results for  $T_{d^{onset}}$  and mass loss of the first degradation step for the non-plasticized raw CA and the externally plasticized CA compounds.

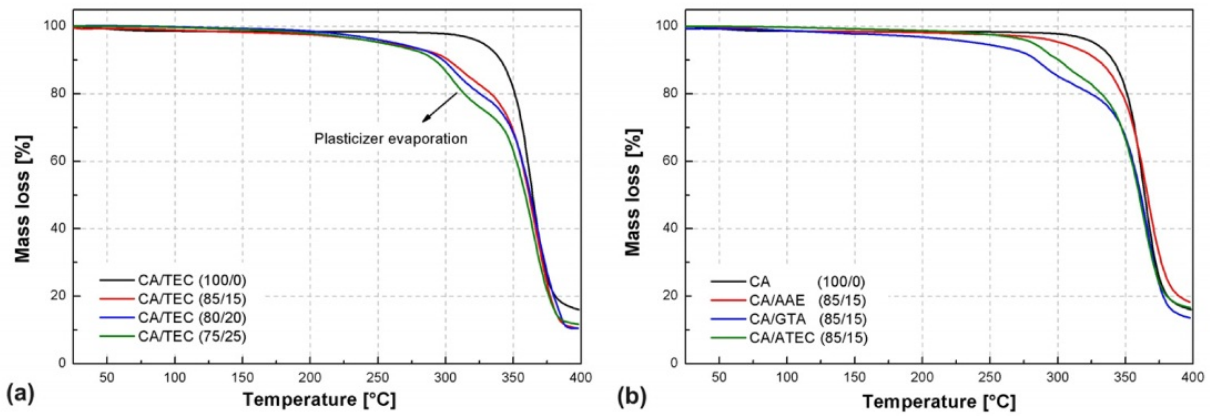
Figure 4 shows typical thermal degradation curves of pure CA and externally plasticized CA as a function of plasticizer content and plasticizer type. Pure, highly substituted CA degrades in one-step with a  $T_{d^{onset}}$  of around 350 °C. CA plasticized with allyl alcohol ethoxylate (AAE) shows one-step degradation similar to pure CA. This plasticizer might influence the thermal stability of CA to a certain extent. A slight decrease in the onset

degradation temperature of CA is observed, as seen in Figure 4 (b) and Table 2. In most cases two-step degradation of externally plasticized CA is observed. The first degradation step is closely linked to the boiling range and evaporation of the plasticizer whereas the second degradation step relates to CA (Table 2). The mass loss in the first degradation step correlates well with the incorporated plasticizer content. With an increase in plasticizer content an increase in mass loss of the first degradation step is observed. As a consequence, most of the plasticizers used do not influence the second degradation step and thermal stability of CA remains almost constant independent of plasticizer content. The plasticizer evaporation and its influence on thermal stability of CA are closely related to its miscibility with CA and its physical properties such as the boiling temperature range. With regard to foam extrusion, early loss of plasticizer during melt processing can lead to drastic changes in the viscosity and the melt strength. As a result, foam extrusion ability of the externally plasticized CA can be significantly reduced. All selected plasticizers, except EGDA, evaporate at temperatures (first degradation step) above the melt processing temperature of CA. The good compatibility and solubility of the selected plasticizers further minimize early evaporation during melt processing of CA. Thus, melt processing properties such as melt rheology can be maintained for the foam extrusion process.

Compound	Plasticizer content [wt.-%]	$T_{d^{onset}}$ [°C] (DIN EN ISO 11358)		Mass loss of 1. step [%]
		1. step	2. step	
CA	0	-	348	-
CA/AAE	15	-	345	no loss of plasticizer
	20	-	343	
	25	-	340	
CA/GDA	15	267	349	14.6
	20	258	347	20.2
	25	242	350	24.0
CA/GTA	15	266	349	16.1
	20	267	350	20.9
	25	248	349	24.3
CA/EGDA	15	186	346	16.2
	20	182	348	21.4
	25	178	349	25.7
CA/TEC	15	293	344	17.4
	20	284	349	20.7
	25	273	345	23.6
CA/ATEC	15	290	352	17.7
	20	279	351	21.0
	25	270	349	23.1

**Table 2.** Onset degradation temperature ( $T_{d^{onset}}$ ) and mass loss of selected externally plasticized CA compounds as a function of plasticizer content (mass loss of 1. step was determined after the isotherm of 6 min at the boiling range).





**Figure 4.** TGA curves (first run without an isotherm of 6 min at the boiling range) of pure non-plasticized CA and plasticized CA: (a) as a function of plasticizer content (TEC) and (b) as a function of plasticizer type at constant plasticizer content (15 wt.-%).

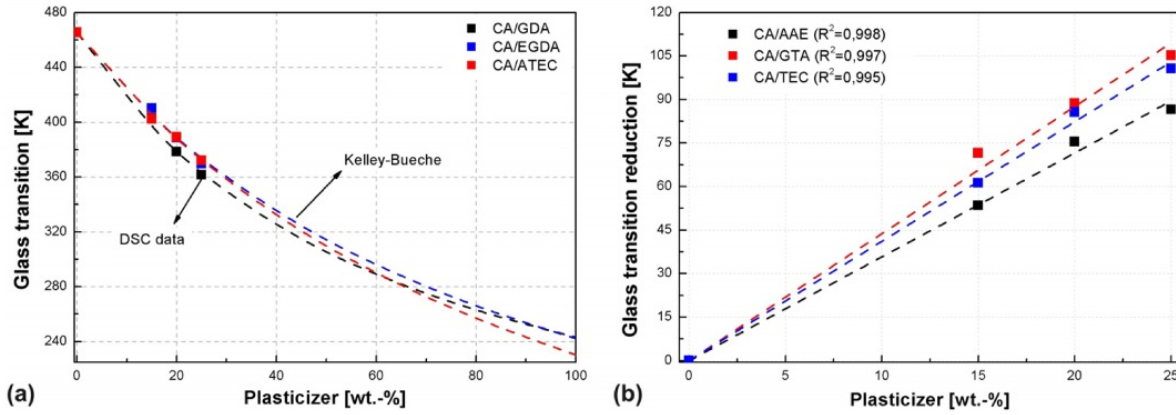
The thermoplasticity and the melt processing range of amorphous polymers are directly linked to their glass transition temperature ( $T_g$ ). Glass transition temperatures of externally plasticized CA were measured by means of differential scanning calorimetry (DSC). Two heating cycles (up to 240 °C) and one cooling cycle (down to -50 °C) were conducted with a heating and cooling rate of 10 K min<sup>-1</sup> and an isotherm of 6 min at the end of each cycle. It is well known that plasticizers can have a tremendous effect on  $T_g$  and consequently on thermoplasticity and melt processing performance of the polymer. Different theories and models exist, which describe the plasticizing principles [40]. In general, the plasticizer diffuses into the polymer matrix and weakens the intermolecular forces between the polymer chains due to shielding effects of functional groups along the chains. The chain mobility increases even at lower temperatures. Thus, glass transition temperature decreases whereas free volume, thermoplasticity, and flow behavior of the polymer increase. The plasticizer efficiency is often expressed by the extent to which a plasticizer reduces a polymer's  $T_g$  [40]. The concentration dependence of the  $T_g$  can be estimated using numerous models such as *Fox* or *Kelley-Bueche* [34, 40]. These models try to correlate the  $T_g$  of the plasticized polymer with the  $T_g$  of the pure polymer and the  $T_g$  of the plasticizer (solvent) respectively. Due to its accuracy in extrapolating the  $T_g$ , the *Kelley-Bueche* model was used to calculate the  $T_g$  of externally plasticized CA according to Eq. (2) [41]

$$T_g = \left[ \frac{(w_1 \cdot T_{g1}) + (K \cdot w_2 \cdot T_{g2})}{w_1 + (K \cdot w_2)} \right] \quad (2)$$

where  $T_g$ ,  $T_{g1}$  and  $T_{g2}$  are the glass transition temperatures of the plasticized polymer, the pure polymer and the plasticizer respectively,  $w_1$  and  $w_2$  are the weight fractions of the polymer and the plasticizer,  $K$  is a constant which can be derived from the densities  $\rho_1$ ,  $\rho_2$  and the thermal expansion coefficients  $\alpha_1$ ,  $\alpha_2$  of the polymer and the plasticizer. By applying the *Simha-Boyer* rule [41] ( $\Delta\alpha \cdot T_g \approx \text{constant}$ ),  $K$  can be simplified according to Eq. (3)

$$K = \frac{\rho_1 \cdot \alpha_2}{\rho_2 \cdot \alpha_1} = \frac{\rho_1 \cdot T_{g1}}{\rho_2 \cdot T_{g2}} \quad (3)$$

As can be seen in Figure 5 (a), calculated values are in good agreement with the experimental data from DSC. An increase in plasticizer content leads to a steady decrease in the  $T_g$  of highly substituted CA due to increase in chain mobility and free volume. There seems to be a linear relationship between plasticizer content and reduction in glass transition temperature within the plasticizer concentration used (15 to 25 wt.-%). Similar results for the glass transition temperature of externally plasticized CA were found in the literature [34, 40, 42].



**Figure 5.** (a)  $T_g$  of externally plasticized CA compounds as a function of plasticizer content and (b) efficiency of selected plasticizers in reducing the  $T_g$  of CA.

The obtained thermal properties for externally plasticized CA confirm the improvements in melt processing from subchapter 2.1. Due to the significant decrease in glass transition while the thermal stability remains almost constant, a considerable improvement in thermoplasticity of externally plasticized CA is achieved. As a result, the melt processing range is enlarged and the thermal degradation of CA during processing is minimized. With respect to foam extrusion, these results are very favorable. The decrease of  $T_g$  accompanied with an unchanged thermal stability of CA not only substantially widens the melt processing range but also the window for the foam extrusion, which will be shown in subchapter 4.

The plasticizer performance depends largely on its compatibility and miscibility with the polymer. Contrary to less compatible plasticizers (e.g. AAE), highly miscible plasticizers such as glycerol triacetate (GTA) or triethyl citrate (TEC) lead to stronger glass transition reduction, as seen in Figure 5 (b). This might be explained by stronger mutual interaction between the functional groups of the plasticizer and CA. A general characterization of the compatibility between a plasticizer and a polymer can be made from the *Hansen* three-dimensional solubility parameter [43], which is defined according to Eq. (4)

$$\delta_t = \sqrt{\delta_h^2 + \delta_d^2 + \delta_p^2} \quad (4)$$

where  $\delta_t$  is the total *Hansen* solubility parameter,  $\delta_h$  is the hydrogen bonding component,  $\delta_d$  is the dispersion component and  $\delta_p$  is the polar component. Table 3 shows the *Hansen* solubility parameter of pure CA and selected plasticizers. Highly substituted CA has a high solubility parameter, and thus it is a polar polymer comparable to polyamide (PA).

Material	$\delta$ [(MPa) <sup>0.5</sup> ]			
	$\delta_t$	$\delta_h$	$\delta_d$	$\delta_p$
CA	25.06	11.00	18.60	12.70
GDA	23.45	14.20	16.40	8.90
GTA	19.37	9.10	16.50	4.50
EGDA	19.51	9.80	16.20	4.70
TEC	20.98	12.00	16.50	4.90
ATEC	19.02	8.60	16.60	3.50

**Table 3.** *Hansen* solubility parameters of CA and selected plasticizers [43].

Following the rule “like dissolves like” it can be assumed that plasticizers with high polarity are favorable for effective plasticization of the polar CA. However, the simplified rule “like dissolves like” is only partially useful due to limitations for polar polymers such as CA or polyamide (PA). Interactions of polar polymers and plasticizers depend more on the presence and arrangement of functional groups along the chains being capable to form donor-acceptor interactions [43]. For good theoretical compatibility with CA, a high polar part of the solubility parameter (energy from dipolar intermolecular force) of the plasticizer is preferred. Due to the free OH-groups of partially substituted CA, hydrogen bonding also plays a significant role in solubility and miscibility. Therefore, a similar hydrogen part of the solubility parameter of the plasticizer is required for improved compatibility with CA. The selected citrate-based plasticizers as well as the acetate-based plasticizers show therefore excellent performance. However, the solubility of the plasticizer and its performance are also determined by a large number of other factors such as its diffusivity, its chemical structure (linear vs. branched) and functional groups. Additionally, molecular properties such as molecular weight or molar volume of the plasticizer are also very important for the plasticizer efficiency. Not only the plasticizer influences the compatibility but also the polymer, its chemical structure, chain flexibility or molecular architecture (amorphous vs. semi-crystalline) have an enormous effect on plasticizer solubility [43].

### 3. Rheological properties

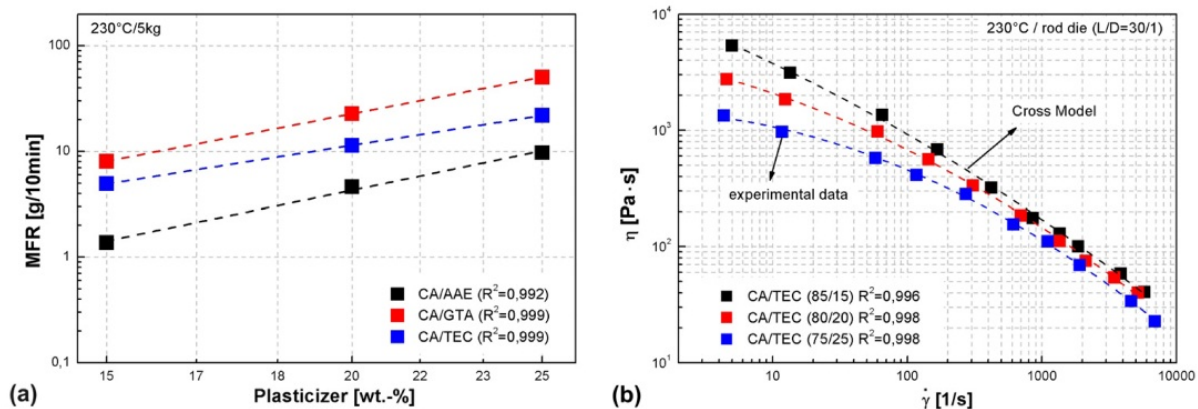
#### 3.1. Influence of plasticizer on melt flow behavior

As described in the introduction, the polymer’s rheology is a key factor for stable foam extrusion processes. Therefore, the rheological properties of externally plasticized CA must be studied when discussing the foamability of this biopolymer. Melt flow behavior and melt viscosity were investigated as a function of plasticizer type and plasticizer content. The melt

flow rate (MFR) was measured at 230 °C and 5 kg load. Melt viscosity was measured by means of high pressure capillary viscometer in a shear rate range typical for extrusion processes. The measurements were carried out at 230 °C with a rod die (L/D of 30/1) and a shear rate ranging from 10 to 3 000 s<sup>-1</sup>. For fitting the experimental data, the well known *Cross Model* was used according to Eq. (5) [44]

$$\eta = \frac{\eta_0}{1 + (\lambda \cdot \dot{\gamma})^{1-n}} \quad (5)$$

where  $\eta_0$  is the zero shear viscosity,  $\lambda$  and  $n$  are fitting parameters and  $\dot{\gamma}$  is the shear rate. Figure 6 (a) shows the melt flow rate (MFR) of externally plasticized CA as a function of plasticizer content and plasticizer type. The obtained relationship between MFR and plasticizer content is similar to the reduction in  $T_g$  and decrease in SME and maximum mass temperature during melt processing. This means, an increase in plasticizer content leads to a steady increase in MFR due to increase in lubricity and chain mobility.



**Figure 6.** (a) MFR of externally plasticized CA compounds as a function of plasticizer type and plasticizer content and (b) melt viscosities of CA plasticized with TEC as a function of shear rate and plasticizer content.

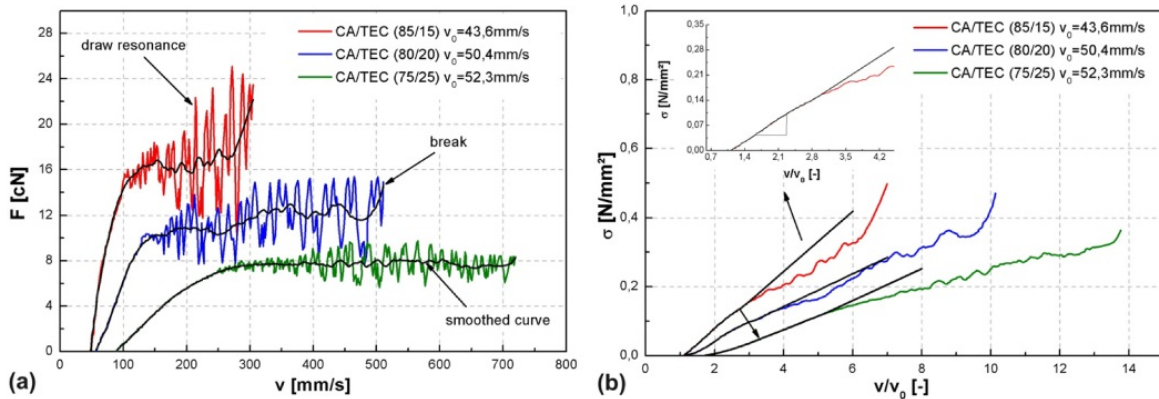
Externally plasticized CA shows typical shear thinning behavior at high shear rates, as seen in Figure 6 (b). By increasing the plasticizer content, a steady decrease in melt viscosity at constant temperature is observed. From Figure 6 (b), one may be also concluded that the influence of plasticizer content diminishes at high shear rates above 1 000 s<sup>-1</sup> due to increased shear thinning. The melt viscosity results agree well with previous results obtained from melt processing (subchapter 2.1) and thermal characterization (subchapter 2.2). With respect to foam extrusion, melt viscosities and melt flow behavior of these externally plasticized CA compounds are in range of typical foam polymers such as PS, branched PE, and branched PP [10, 11, 15, 45, 46].

### 3.2. Influence of plasticizer on melt strength and melt extensibility

Besides melt viscosity, information about melt strength and melt elasticity is crucial for foam extrusion as both factors are important when discussing foam expansion, foam stability and



foam collapse [47]. Therefore, rheotens tests were conducted using a rheograph with rheotens device from Göttfert. Melt strands were extruded through a single screw extruder using a rod die with an L/D of 30/2 and a constant throughput of  $0.5 \text{ kg h}^{-1}$  at  $220^\circ\text{C}$ . The extruded melt strands were grabbed and draw-down by a pair of rotating wheels fixed to the rheotens analyzer. The draw-down velocity of the extruded melt strand was then steadily increased with a constant acceleration rate of  $24 \text{ mm s}^{-2}$ . Detailed information on the rheotens test can be found in [48]. Figure 7 shows rheotens curves obtained for externally plasticized CA melts. The plasticizer content and the plasticizer type significantly influence the strength and drawability (extensibility) of the CA melt. An increase in plasticizer content leads to a decrease in draw-down force  $F$  (melt strength) while a tremendous increase in melt extensibility is observed. Highly compatible plasticizers behave like good solvents. As a result, intermolecular forces within the polymer network decrease whereas chain mobility increases. The polymer chains can then be easily disentangle and aligned in draw-down direction. As a consequence, the draw-down force  $F$  as well as the stress  $\sigma$  decrease whereas the melt extensibility drastically increases. The typical draw resonance, which is seen in Figure 7 (a), is also reduced due to better flow and chain orientation in draw-down direction. The initial slope (melt stiffness) manually obtained from the stress curves also steadily decreases with increasing plasticizer content, as seen in Figure 7 (b).



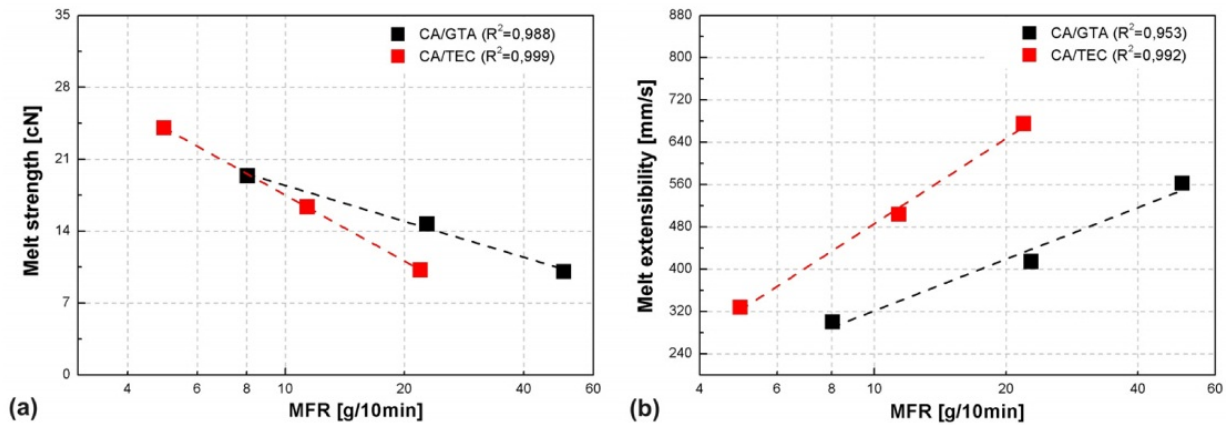
**Figure 7.** (a) Draw-down force  $F$  as a function of draw-down velocity  $v$  of CA plasticized with TEC in dependence of plasticizer content and (b) draw-down stress  $\sigma$  as a function of draw ratio  $v/v_0$  in dependence of plasticizer content.

Figure 8 shows the correlation between the melt flow rate (MFR) and the melt strength as well as the melt extensibility for CA plasticized with glycerol triacetate (GTA) and triethyl citrate (TEC).

With increasing melt flow rate (MFR) of externally plasticized CA, a continuous decrease of melt strength was found while melt extensibility steadily increases. An explanation for the good melt elasticity and melt strength could be the polydispersity of CA due to its natural character and the two-step esterification process [49, 50]. Polydispersity or bimodality, being attributed to a mixture of short and long chains and/or branched and linear chains, generally favors high melt strength and strain hardening [4]. The polydispersity index ( $M_w/M_n$ ) of the pure CA used in this study was measured by means of gel permeation chromatography (GPC) with PS standards in THF solution. Three samples of the pure CA



were measured. Table 4 shows the obtained values for  $M_n$  and  $M_w$  as well as  $M_w/M_n$  for the non-plasticized raw CA and for selected externally plasticized CA compounds. The observed polydispersity index ranges from 3 to 5. This is comparable to branched PP [12, 51] or blends of different types of PS [15, 52].



**Figure 8.** Correlation of the melt flow rate (MFR) with (a) the melt strength and (b) the melt extensibility of externally plasticized CA compounds as a function of plasticizer.

Compound	Plasticizer content [wt.-%]	$M_n$ [g mol <sup>-1</sup> ]	$M_w$ [g mol <sup>-1</sup> ]	$M_w/M_n$
CA (Sample 1)	0	45 180	204 410	4.5
CA (Sample 2)		56 045	266 460	4.8
CA (Sample 3)		40 135	161 950	4.0
CA/AAE	15	53 948	225 300	4.2
	20	54 851	241 370	4.4
	25	51 769	251 590	4.8
CA/GDA	15	51 922	223 080	4.3
	20	43 790	197 480	4.5
	25	45 970	221 280	4.8
CA/TEC	15	44 695	173 730	3.9
	20	56 948	230 680	4.1
	25	44 860	201 770	4.5

**Table 4.** Number average molecular weight  $M_n$ , weight average molecular weight  $M_w$  and polydispersity index of pure CA and selected externally plasticized CA compounds.

Due to the polydispersity and the strong intermolecular interaction between the free OH-groups of partially substituted CA, certain intrinsic melt strength of this biopolymer is given. The observed high melt extensibility for highly plasticized CA is excellent with respect to foam extrusion. It means that multi-axial stretching of the externally plasticized CA melt during foam expansion (cell growth) is possible without breakage of the thin cell walls. Nevertheless, the melt stiffness, which is the maximum melt strength (draw-down

force), and the melt stress are comparably low at a high plasticizer content of 25 wt.-%. This can lead to instabilities in the foam network during foaming and foam collapse can occur due to low cell wall stiffness. This problem can be overcome by keeping the plasticizer content below ca. 20 wt.-%. With this reduced content, melt strength of 15 to 20 cN can be achieved while melt extensibility remains at a high level of 400 to 600 mm s<sup>-1</sup>. These values are excellent for an externally plasticized polymer and agree well with results for non-plasticized foam polymers such as PE, PP, and PS [13, 48, 53].

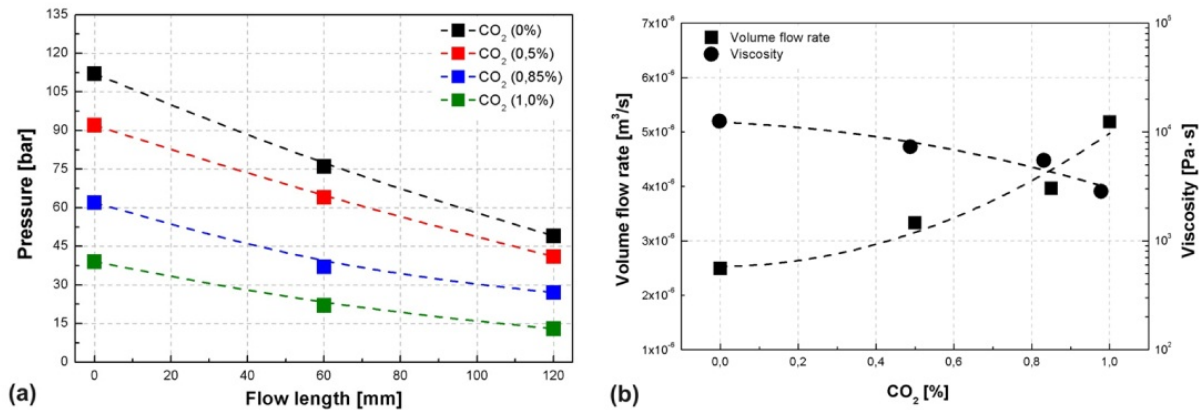
As a conclusion, the obtained results show that the properties studied are closely linked together and strongly influenced by the plasticizer content as well as by the type of plasticizer used. From these results, it can be concluded that the lower the glass transition of the amorphous externally plasticized CA compounds while the thermal stability remains constant, the wider the window for thermoplastic processing and the easier it will be to adjust the melt rheology of CA to the requirements for the foam extrusion process. The significantly enlarged melt processing range means at the same time a considerable broadening of the window for the foam extrusion. However, if the plasticizer content is too high, melt stiffness and melt strength may become too low for stable foam extrusion processes. By changing the plasticizer content or by using a more miscible plasticizer, excellent melt processing behavior as well as good thermal and rheological properties of CA can be achieved for foam extrusion. To proof the foam extrusion behavior, preliminary foam extrusion tests were conducted. For these tests, an externally plasticized CA compound with 20 wt.-% of glycerol triacetate (GTA) was produced because of a good balance between melt processing, melt flow, melt extensibility, and melt strength. The compound were prepared by means of a co-rotating twin-screw extruder (TSA EMP 26-40) with an L/D of 40/1. The screw speed was set at 250 rpm and the throughput was fixed at 10 kg h<sup>-1</sup>. The temperature profile ranged from 160 °C at the feeding zone to 205 °C at the die. The compound was dried for 24 h at 70 °C (hot air dryer).

### 3.3. Influence of physical blowing agent on melt flow behavior

As pointed out in the introduction, the blowing agent also strongly influences the melt rheology of the polymer during foam extrusion. Therefore, information on gas loaded CA melts is essential for setting the right foam extrusion parameters such as the temperature of the extruder. It is well known that the PBA can act as a plasticizer or solvent [16-18]. The extent to which a PBA influences the rheology and the thermal properties of the polymer is directly related to its physical properties such as molar mass, solubility and diffusivity in the polymer melt. The influence of blowing agent on the flow behavior of a CA melt plasticized with 20 wt.-% GTA was studied by means of in-line rheometer with high speed camera system. These preliminary investigations were carried out on a 60 mm single screw extruder with an L/D of 40/1 (Barmag Oerlikon Textile GmbH & Co. KG). Carbon dioxide (CO<sub>2</sub>) was selected as an eco-friendly PBA. The slit die gap of the rheometer was fixed at 5 mm and the throughput of the single screw extruder was kept constant at 11 kg h<sup>-1</sup>.

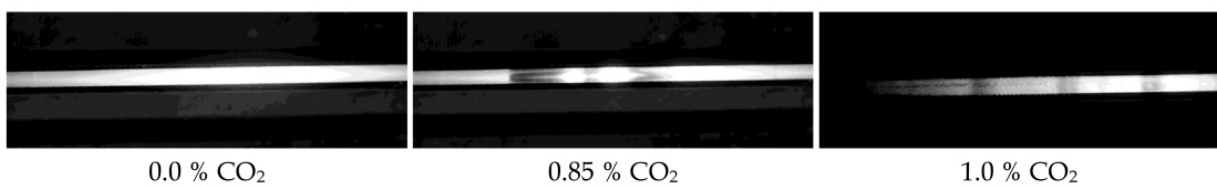
As seen from Figure 9, pressure decreases continuously over the flow length for the externally plasticized CA melt. When carbon dioxide is added to the externally plasticized CA melt, an

overall shift of the pressure curve to lower values is observed. A continuous increase in carbon dioxide content leads to a steady decrease in the pressure curve over flow length. The shape of the pressure curve seems to be independent from the carbon dioxide content. The plasticization effect of carbon dioxide used as PBA is not only seen in the pressure decrease but also confirmed by a decrease in viscosity and increase in volume flow of the externally plasticized CA melt at constant processing conditions (temperature, throughput, slit die gap).



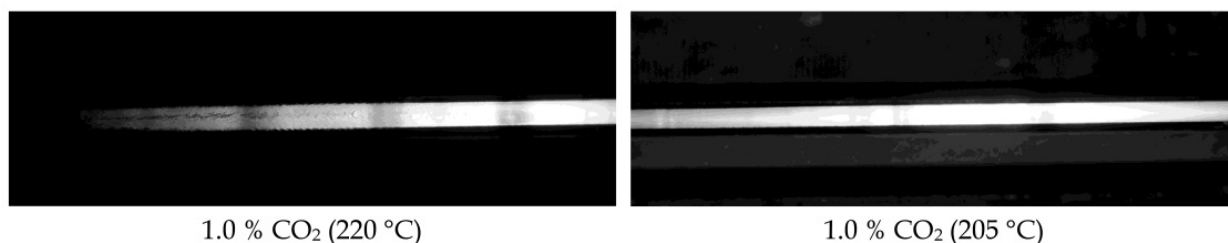
**Figure 9.** (a) Pressure distribution and (b) volume flow rate and viscosity of CO<sub>2</sub> loaded CA melt plasticized with 20 wt.-% GTA as a function of flow length and CO<sub>2</sub> content at constant rheometer temperature (220 °C) and constant processing parameters.

Since the effective dissolution of a PBA in the polymer melt is mostly pressure controlled, a certain viscosity of the polymer melt is required to achieve sufficient pressure in the extruder for dissolution of the PBA. As seen in Figure 10, due to the constant processing parameters (throughput, slit die gap, rheometer temperature), partial supersaturation and premature separation of carbon dioxide from the externally plasticized CA melt is observed, especially at 1 % CO<sub>2</sub> (on weight basis). An explanation for this could be the continuous increase in volume flow and decrease in melt viscosity. As a result, the pressure inside of the extruder is too low to keep carbon dioxide dissolved in the CA melt.



**Figure 10.** Influence of CO<sub>2</sub> content on supersaturation of CO<sub>2</sub> from the CA melt plasticized with 20 wt.-% GTA and pnenucleation in the in-line rheometer at constant rheometer temperature (220 °C) and constant processing parameters.

To minimize premature supersaturation of carbon dioxide and to avoid pnenucleation in the extruder, the temperature of the extruder and the rheometer can be reduced. This leads to an increase in the viscosity of the gas loaded CA melt. As a result, the pressure in the extruder also increases, keeping the carbon dioxide dissolved in the CA melt and avoiding premature supersaturation in the extruder. This is clearly shown in Figure 11.



**Figure 11.** Effect of rheometer temperature on supersaturation of 1 % CO<sub>2</sub> from the CA melt plasticized with 20 wt.-% GTA at constant throughput (11 kg h<sup>-1</sup>) and slit die gap (5 mm).

The results for carbon dioxide used as a PBA show the general complexity between gas loaded polymer melts and the extrusion process. To get more information on the melt flow and viscosity behavior of gas loaded externally plasticized CA melts, further studies have to be conducted using additional blowing agents, for example butane or nitrogen (N<sub>2</sub>).

#### 4. Foam extrusion of externally plasticized cellulose acetate

For the preliminary foam extrusion tests, the same CA compound composition (20 wt.-% GTA) as in subchapter 3.3 was used because of a good balance between melt processing and relevant melt rheology. Extrusion foamed CA rods were produced with different physical blowing agents (PBA). Table 5 shows the PBAs used for these preliminary foam extrusion tests.

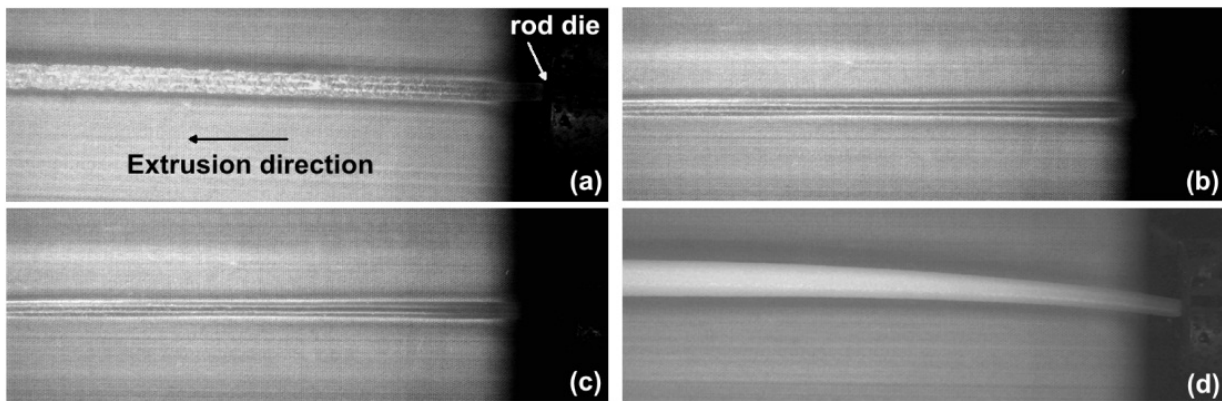
Property	CO <sub>2</sub>	N <sub>2</sub>	n-butane	trans-1,1,1,3-tetrafluoropropene (HFO 1234ze)
Molar mass [g mol <sup>-1</sup> ]	44.0	28.0	58.1	114.0
Boiling point [°C]	-78.5	-195.79	-0.5	-19.0
Critical temperature [°C]	31.0	-146.9	149.9	382.51
Critical pressure [MPa]	7.38	3.4	3.8	3.63
Vapor pressure (25 °C) [MPa]	6.43	-	0.24	0.49
GWP	1	-	3	6

**Table 5.** Physical blowing agents used and some short characteristics.

Additionally, a 5 % talc masterbatch based on the externally plasticized CA compound was added at 0.2, 0.6 and 0.8 wt.-% to investigate the influence of this nucleating agent on the foam morphology. The talc used has platelet geometry with a diameter  $d_{0.5}$  of 2  $\mu\text{m}$ . The physical foam extrusion tests were carried out on a 60 mm single screw extruder with an L/D of 40/1 (Barmag Oerlikon Textile GmbH & Co. KG). The extruder is equipped with a mixing screw optimized for the foam extrusion process. The last 11 D of L before the die are temperature controlled in order to cool the polymer melt. The blowing agent was compressed and injected into the extruder barrel through a pressure hole at 16 D of L using

a metering system equipped with a diaphragm pump. By means of a static mixer, the PBA is dispersed in the melt.

As seen from Figure 12, the blowing agent not only influences the melt rheology of CA but also the foam extrusion and expansion behavior at the die.

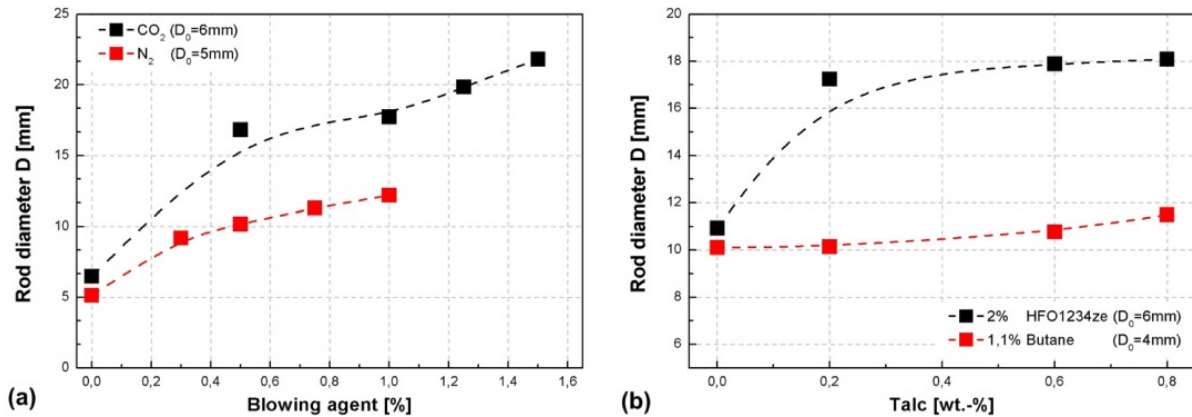


**Figure 12.** Influence of blowing agent and nucleating agent content on foam extrusion process of CA plasticized with 20 wt.-% GTA: (a) 1 % CO<sub>2</sub> + 0 wt.-% talc, (b) and (c) 2 % HFO 1234ze + 0 wt.-% talc and (d) 2 % HFO 1234ze + 0.6 wt.-% talc.

Carbon dioxide shows rapid expansion at the die in comparison to HFO 1234ze. An explanation for this could be the higher diffusivity and permeability of carbon dioxide due to its lower molecular size when compared to longer chain PBAs such as HFO 1234ze. Blowing agents having a high diffusivity will be phased out in a shorter time [54]. Additionally, the solubility of carbon dioxide is restricted in most polymer melts when compared to other conventional blowing agents such as hydrofluorocarbons [54]. High pressure in the extruder is required to keep carbon dioxide dissolved in the externally plasticized CA melt. The high pressure gradient at the die in combination with the high vapor pressure and high diffusion rate of carbon dioxide causes a strong expansion process at the die. Not only the PBA but also the addition of nucleating agents, for example talc, affects the foaming behavior at the die. By adding talc to HFO 1234ze, the foaming process of externally plasticized CA is significantly improved that can be seen in Figure 12 (c) and (d). The expansion directly starts at the die due to better nucleation (more and faster nucleation) in conjunction with stable cell growth as both processes start simultaneously.

The investigation of the rod diameter ( $D$ ) and the foam density as a function of PBA content and talc content verify the results got from high speed camera images. As seen in Figure 13, a steady increase in  $D$  is observed with increasing concentration of PBA. Generally, the higher the PBA concentration, the more PBA is dissolved in the polymer melt that can cause stronger foaming. The type of PBA and its solubility in the externally plasticized CA melt influences the intensity of the slope. The addition of talc used as a nucleating agent shows a selective influence. For butane no significant influence is observed whereas for HFO 1234ze the addition of talc (0.2 wt.-%) significantly improves the foam expansion process. This is in good agreement with the visual results obtained with the high speed camera system.





**Figure 13.** (a) Influence of PBA content on rod diameter ( $D$ ) of CA rods foamed with CO<sub>2</sub> and N<sub>2</sub> and (b) rod diameter ( $D$ ) of CA rods foamed with butane and HFO 1234ze as a function of talc content at constant PBA content.

From Figure 13 one may also conclude that an increase in nucleating agent content from 0.2 to 0.8 wt.-% does not affect the rod diameter considerably. An explanation for this could be the heterogeneous nucleation process in presence of talc. Therefore, the cell nucleation predominates the cell growth. Contrary, homogeneous nucleation occurs in absence of talc. Consequently, cell nucleation rate is limited and the following cell growth process predominates. The nucleating agent is therefore more important for controlling the nucleation rate, the cell density, the foam morphology, and the stabilization of the foam network. It is one parameter that significantly affects the foam density and foam ratio, this is the ratio between the density of the foamed and the unfoamed polymer. As expected, increasing talc content leads to a steady decrease in foam density and continuous increase in the foam ratio, as shown in Table 6. These observations agree well with results from literature [55, 56]. However, too high talc contents can lead to agglomeration effects of the nucleated cells [57, 58] or can cause cell collapse [59]. Therefore, an increase in foam density and a decrease in foam ratio may occur at too high talc contents [60].

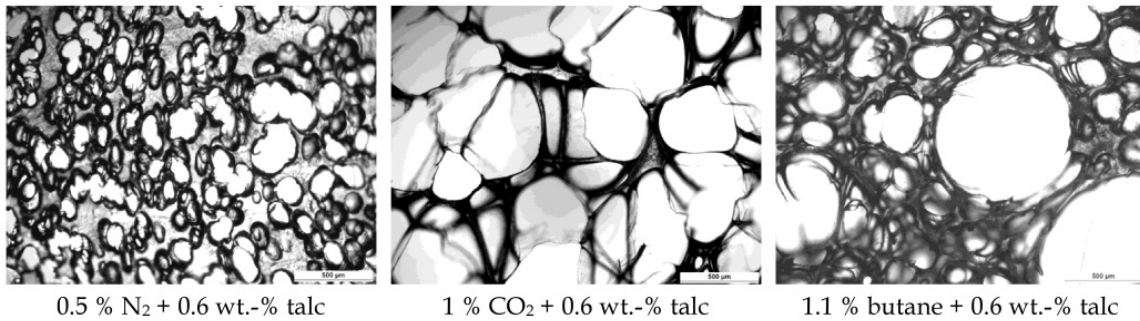
The influences of PBA and talc on the foaming process, the foam density, and the foam ratio are supported by investigations of the foam morphology using optical microscopy (OM). Figure 14 shows selected microscopy images of extrusion foamed CA rods.

Butane as well as nitrogen causes a coarse inhomogeneous morphology with a broad cell size distribution and large partially opened cells to some extent. This can be explained by premature phase separation (supersaturation) and cell coalescence due to the poor solubility of butane and nitrogen in the externally plasticized CA melt. Li [61] found that less soluble blowing agents tend to diffuse out more rapidly than the more soluble one. Consequently a smaller amount of these blowing agents is dissolved in the polymer melt for foaming. By comparison, 1 % CO<sub>2</sub> with 0.6 wt.-% talc shows uniform closed cell morphology with homogeneous cell distribution and thin cell walls. These investigations agree well with the detected foam density and foam ratio. Scanning electron microscopy (SEM) images are of further evidence of the previous results. Blowing agents which show limited solubility in the externally plasticized CA melt such as butane or nitrogen lead to heterogeneous foam morphologies with large and partially opened cells, which is seen in Figure 15 (b). These large

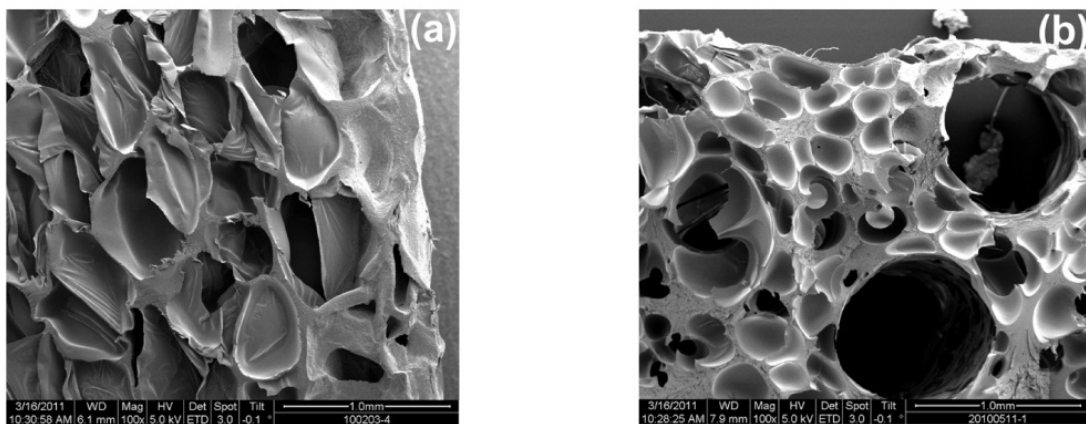
cells can act as voids. As a result, final properties such as mechanical performance of these foams may be poor when compared to foams which have a fine and uniform morphology.

Blowing agent	Content [%]	Talc content [%]	Density [ $\text{kg m}^{-3}$ ]	Foam ratio [-]
-	-	-	1310	1.0
CO <sub>2</sub>	0.5	0.0	262	5.0
	1.0		178	7.4
	1.25		140	9.4
	1.5		105	12.5
	1.0	0.2	162	8.1
		0.6	152	8.6
		0.8	124	10.6
Butane	1.1	0.0	351	3.7
		0.2	332	3.9
		0.6	322	4.1
		0.8	271	4.8
	1.3	0.8	213	6.2

**Table 6.** Density and foam ratio of extruded CA foam rods as a function of PBA and talc.



**Figure 14.** Influence of blowing agent on the foam morphology of selected CA foam rods at constant talc content (0.6 wt.-%) [OM, transmitted light, magnification 50x].



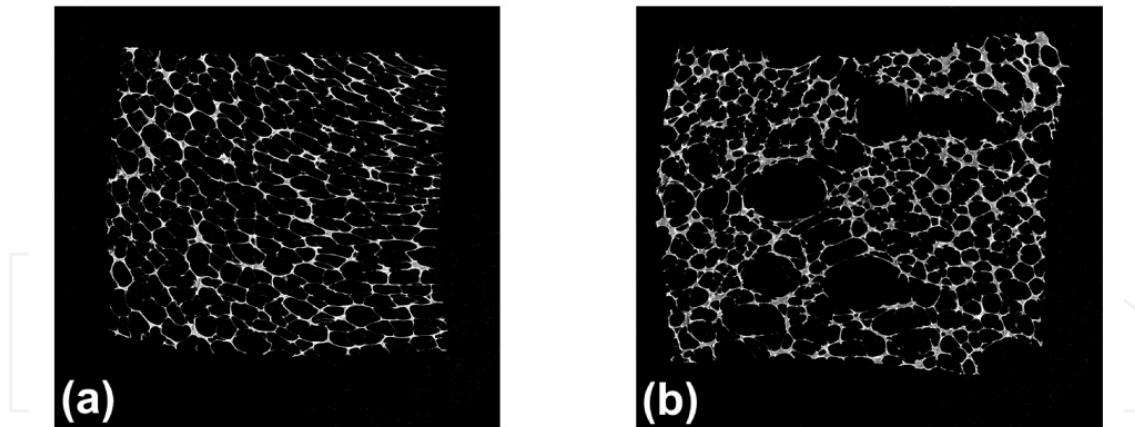
**Figure 15.** Influence of blowing agent on the foam morphology of selected CA foam rods at constant talc content (0.8 wt.-%) for (a) 1 % CO<sub>2</sub> and (b) 1.1 % butane (SEM, magnification 100x).

The limited solubility of butane and nitrogen can be explained by their nonpolar character. As seen from Table 7, only the dispersion part of the *Hansen* solubility parameter is accessible for dissolving butane and nitrogen in the polar externally plasticized CA melt. In contrast, carbon dioxide is a more polar or hydrogen bonding gas. Therefore, the polar part and hydrogen bonding part are also available for dissolution of carbon dioxide in the CA melt.

PBA	$\delta$ [(MPa) <sup>0.5</sup> ]			
	$\delta_t$	$\delta_h$	$\delta_d$	$\delta_p$
CO <sub>2</sub>	17.4	5.8	15.6	5.2
N <sub>2</sub>	11.9	0.0	11.9	0.0
Butane	14.1	0.0	14.1	0.0

**Table 7.** *Hansen* solubility parameter of selected physical blowing agents [43].

Micro-CT measurements of selected CA foam rods are shown in Figure 16. These images confirm the results from OM and SEM. For butane, cell coalescence and partially opened cell structures are evident, especially in the center of the sample cross-section. Similar results were obtained for nitrogen. Due to the limited solubility in the externally plasticized CA melt, premature supersaturation of butane and nitrogen from the melt occurs. Thus, coalescence primarily in the flow center is observed due to this being the area of the lowest flow resistance. Conversely, carbon dioxide causes fine cell morphology with homogeneous cell size distribution and high cell density across the sample.

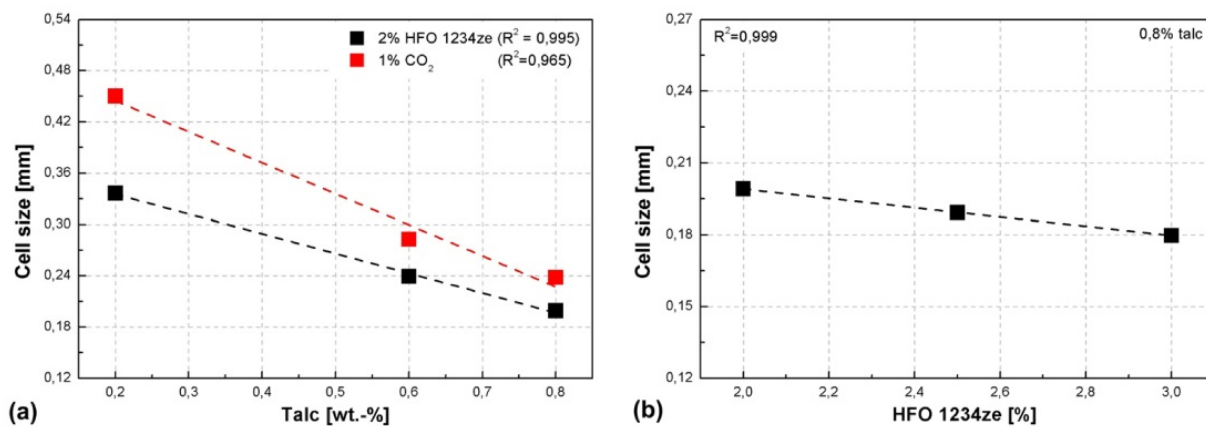


**Figure 16.** Influence of blowing agent on the foam morphology of selected CA foam rods at constant talc content (0.8 wt.-%) for (a) 1 % CO<sub>2</sub> and (b) 1.1 % butane (Micro-CT, 2D cross-sections).

To obtain further information about the influence of the blowing agents and the nucleating agent, cell size and cell density ( $N_f$ ) were studied. Cell density ( $N_f$ ) in cells cm<sup>-3</sup> was calculated according to Eq. (6) [62]

$$N_f = \left( \frac{N}{A} \right)^{\frac{3}{2}} \quad (6)$$

where  $N$  is the number of cells and  $A$  is the area in  $\text{cm}^2$ . As expected from literature [55, 60], the addition of a nucleating agent such as talc leads to a considerable decrease in cell size (Figure 17). This is in good agreement with the obtained results for the foam density and foam ratio. From Figure 17, one may conclude that no tremendous influence of the PBA concentration on the cell size was found at a talc content of 0.8 wt.-% within the range of PBA concentration studied. Similar results were found in [55] for PP foamed with carbon dioxide above 0.8 wt.-% talc content. It can be assumed that heterogeneous cell nucleation predominates in presence of talc and therefore cell nucleation rate is controlled by the high talc content regardless of the increase in concentration of the PBA used.



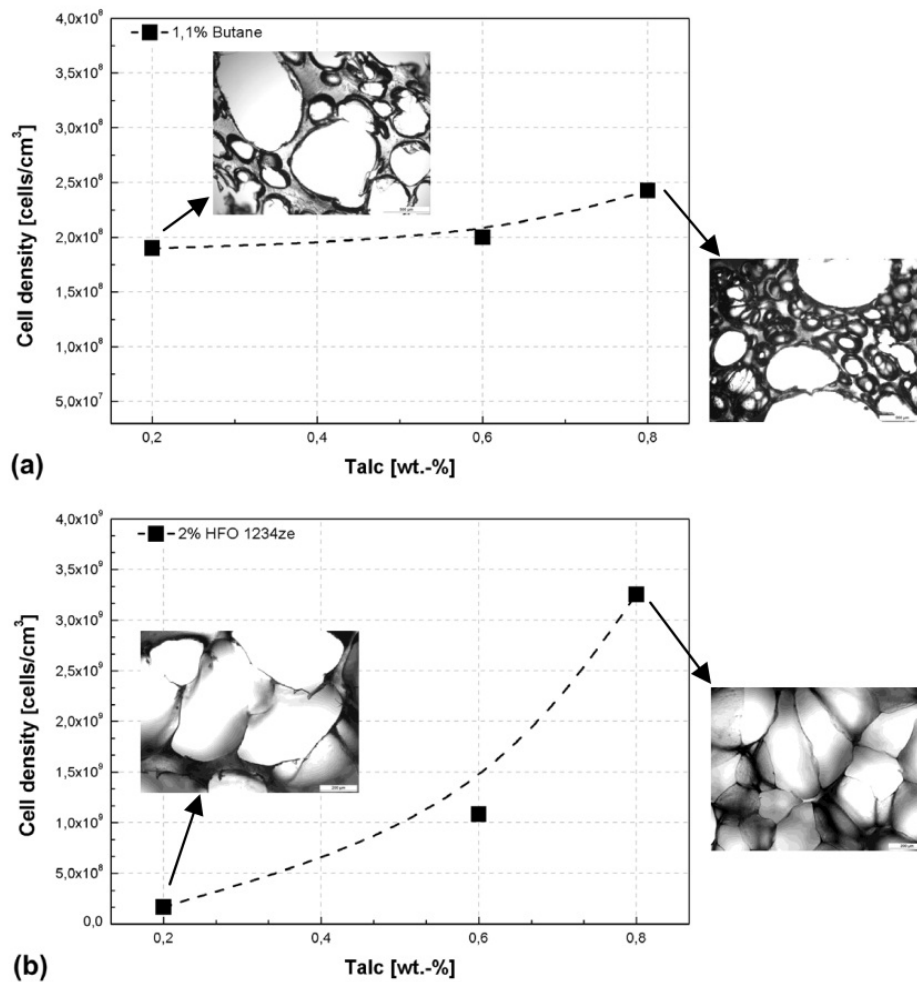
**Figure 17.** (a) Cell size of extruded CA rods foamed with 1 %  $\text{CO}_2$  and 2 % HFO 1234ze as a function of talc content and (b) as a function of HFO 1234ze concentration at 0.8 wt.-% talc.

As the cell size continuously decreases with increasing talc content, cell density basically increases at the same time due to higher cell nucleation rate. This is shown in Figure 18. For HFO 1234ze, which shows good solubility in the externally plasticized CA melt, an exponential increase in cell density is observed with continuous increase in talc content due to an increase in heterogeneous cell nucleation rate. The higher cell density is directly seen in the finer foam morphology. In contrast, no excessive increase in cell density is observed for butane even at 0.8 wt.-% talc. This agrees well with the previous results obtained for the foam density, the foam ratio, and the foam morphology. Due to the limited solubility of butane, premature supersaturation of butane from the externally plasticized CA melt occurs. As a result, only small amount of butane remains dissolved in the CA melt for foaming at the die. This is directly seen in almost unchanged foam morphologies of the extruded CA rods foamed with 1.1 % butane at 0.2 wt.-% talc and 0.8 wt.-% talc respectively.

Figure 19 (a) shows the relationship between cell size and cell wall thickness. Completely different results are obtained for the selected PBAs, which might be attributed to their solubility in the externally plasticized CA melt. For butane, which shows limited solubility in externally plasticized CA melt, only a slight change in average cell size within the selected talc content is observed. The cell wall thickness of the extruded CA rods foamed with butane is also significantly higher when compared to HFO 1234ze, even at high talc content of 0.8 wt.-%. Similar results were obtained for nitrogen. The limited solubility of

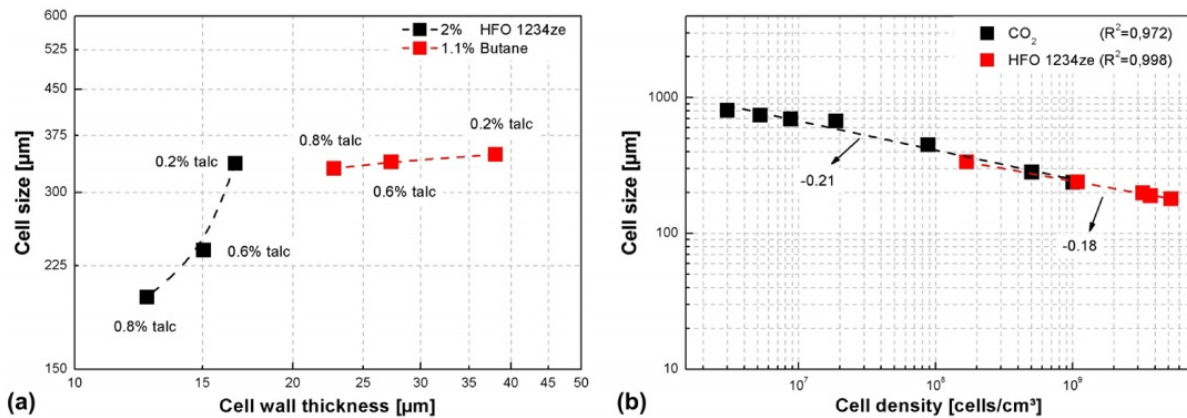


butane and nitrogen leads to premature supersaturation. As a result, insufficient amount of these blowing agents are dissolved in the externally plasticized CA melt for cell nucleation and cell growth. Contrary, HFO 1234ze shows good solubility in the externally plasticized CA melt. Consequently, a significant decrease in cell size with increasing talc content is observed. Furthermore, the cell wall thickness decreased continuously with decreasing cell size. This is in good agreement with the literature [63]. Figure 19 (b) shows the relationship between cell size and cell density in a LOG-LOG plot. A linear relationship between cell size and cell density is observed. The values of the slopes obtained by linear fit are close to values obtained by Ito [63] for polycarbonate-based nanocomposite foams.



**Figure 18.** Influence of talc content on cell density ( $N_f$ ) of extruded CA rods foamed (a) with 1.1 % butane and (b) with 2 % HFO1234ze.





**Figure 19.** (a) Cell size in dependence of cell wall thickness as a function of talc content and PBA type and (b) cell size in dependence of cell density for extruded CA rods foamed with CO<sub>2</sub> and HFO 1234ze.

As a conclusion, the preliminary foam extrusion tests showed that externally plasticized CA is a promising biopolymer for foam extrusion technologies. By choosing an appropriate plasticizer type, the optimal plasticizer content, and a suitable blowing agent, highly substituted CA exhibits good foam extrusion behavior. Properties of CA foam rods such as foam density, foam ratio or cell density are in range with other polymers foamed with similar low PBA concentrations and similar talc contents [55]. Further improvements of the foam extrusion of externally plasticized CA can be achieved by either increasing the amount of PBA or by using higher talc content. The use of CBA/PBA mixtures as well as the use of nano-scaled particles as nucleating agents may lead to additional improvements in the foam extrusion behavior and final foam properties. Park [64] showed that the addition of nanoclays to the foam process produces finer foam morphologies with higher cell densities and foam ratios due to accelerated cell nucleation and suppressed cell coalescence.

## 5. Conclusions

In this chapter the use of externally plasticized CA for foam extrusion with physical blowing agents was discussed. Properties relevant to the foamability of externally plasticized CA were presented. The influence of plasticizer type, its content, and its miscibility with CA was studied with respect to the requirements for foam extrusion. An increase of plasticizer content leads to a steady decrease in glass transition temperature while the thermal stability of CA remains almost constant. Glass transition temperature of externally plasticized CA decreases about 100 °C when 25 wt.-% of a highly miscible plasticizer, for example TEC or GDA, is added. The melt processing range of the amorphous compounds increases significantly and thermoplasticity is improved over a wide temperature range. Not only the melt processing but also the melt rheology, the melt strength, and the melt extensibility are considerably improved. The polydispersity of CA as well as the strong intra- and intermolecular interactions between the free OH-groups promote high melt strength and high melt extensibility. Melt strength and melt extensibility are in range of conventional foam polymers such as PS or branched PP. If the plasticizer content is too high, melt strength and melt stiffness of the CA compounds are too low with respect to foam network stabilization. This can be overcome by reducing the plasticizer content. When choosing a

more compatible plasticizer, similar results can be achieved even at lower plasticizer content. This is very important with regard to the prevention of extensive plasticizer evaporation during melt processing, which is often combined with drastic changes in the properties required for the foam extrusion process. The use of highly miscible plasticizers also minimizes the well known problem of plasticizer migration. Acetate-based plasticizers such as GDA, GTA, and EGDA as well as citrate-based plasticizers such as TEC and ATEC showed excellent miscibility with CA. Approximately 20 wt.-% of these plasticizers were found to be a good concentration in order to achieve a balanced property profile and to fulfill the specifications for foam extrusion. Physical foam extrusion tests of CA externally plasticized with 20 wt.-% GTA were conducted to proof the usability of thermoplastic CA for foam extrusion. Different PBAs, namely carbon dioxide, nitrogen, butane, and trans-1,1,1,3-tetrafluoropropene (HFO 1234ze), were studied. Talc was added as a nucleating agent. It was found, that the type of PBA and its concentration used as well as the nucleating agent content have tremendous effects on the foam extrusion behavior, the foam morphology, and the final foam properties such as foam density, cell size, and cell density. When butane and nitrogen are used as blowing agents only limited foam extrusion performance is achieved. An explanation for this could be the limited solubility of these blowing agents in the externally plasticized CA melt. By comparison, carbon dioxide and HFO 1234ze seems to be suitable blowing agents for externally plasticized CA. Both, carbon dioxide and HFO 1234ze, lead to good foam extrusion behavior and excellent expansion at the die. When talc is added as a nucleating agent this significantly improves the foam morphologies and the final foam properties. An increase in talc content leads to finer and more homogeneous foam morphologies, higher cell densities, smaller cells, and thinner cell walls. As a conclusion, externally plasticized CA foamed with carbon dioxide or HFO 1234ze in presence of talc shows excellent foam extrusion performance. Foam morphologies, cell densities, and cell sizes are comparable to conventional polymers such as PP, PS or polyesters that are foamed with similar low blowing agent content and comparable nucleating agent content. With respect to its property profile, externally plasticized CA is a promising bio-based polymer for foam extrusion and for replacing conventional oil-based polymers, especially PS, in certain foam applications.

## Author details

Stefan Zepnik

*Fraunhofer Institute for Environmental, Safety, and Energy Technology UMSICHT, Oberhausen, Germany*

*Center of Engineering Sciences, Martin Luther University, Germany*

Tilo Hildebrand

*Institute of Plastics Processing (IKV), RWTH Aachen University, Aachen, Germany*

Stephan Kabasci and Thomas Wodke

*Fraunhofer Institute for Environmental, Safety, and Energy Technology UMSICHT, Oberhausen Germany*

Hans-Joachim Radusch

*Center of Engineering Sciences, Martin Luther University, Germany*

## Acknowledgement

This work was funded by the Federal Ministry of Food, Agriculture and Consumer Protection BMELV and the Agency for Renewable Resources FNR.

## 6. References

- [1] Eaves D. (2004) Handbook of Polymer Foams. Shawbury: Smithers Rapra Technology Limited. 304 p.
- [2] Zhang Q., Xanthos M. (2004) Material Properties Affecting Extrusion Foaming. In: Lee S.-T., Ramesh N.S., editors. Polymeric Foams: Mechanisms and Materials. Boca Raton: CRC Press. pp. 111-138.
- [3] Lee S.-T. (2000) Introduction. In: Lee S.-T., editor. Foam Extrusion: Principles and Practice. Boca Raton: CRC Press. pp. 1-14.
- [4] Gendron R. (2005) Rheological Behavior Relevant to Extrusion Foaming. In: Gendron R., editor. Thermoplastic Foam Processing: Principles and Development. Boca Raton: CRC Press. pp. 56-116.
- [5] Gendron R., Daigneault L.E. (2000) Rheology of Thermoplastic Foam Extrusion Process. In: Lee S.-T., editor. Foam Extrusion: Principles and Practice. Boca Raton: CRC Press. pp. 35-80.
- [6] Liao R., Yu W., Zhou C. (2010) Rheological Control in Foaming Polymeric Materials: Part 1. Amorphous Polymers. *Polymer*. 51: 568-580.
- [7] Stange J. (2006) Einfluss rheologischer Eigenschaften auf das Schäumverhalten von Polypropylenen unterschiedlicher molekularer Struktur. PhD Thesis. 201 p.
- [8] Gunkel F., Spörrer A.N.J., Lim G.T., Bangarusampath D.S., Altstädt A. (2008) Understanding Melt Rheology and Foamability of Polypropylene-Based TPO Blends. *J. Cell. Plast.* 44: 307-325.
- [9] Yamaguchi M. (2004) Melt Elasticity of Polyolefins: Impact of Elastic Properties on Foam Processing. In: Lee S.-T., Ramesh N.S., editors. Polymeric Foams: Mechanisms and Materials. Boca Raton: CRC Press. pp. 19-72.
- [10] Stange J., Münstedt H. (2006) Effect of Long-chain Branching on the Foaming of Polypropylene with Azodicarbonamide. *J. Cell. Plast.* 42: 445-467.
- [11] McCallum T.J., Kontopoulou M., Park C.B., Muliawan E.B., Hatzikiriakos S.G. (2007) The Rheological and Physical Properties of Linear and Branched Polypropylene Blends. *Polym. Eng. Sci.* 47: 1133-1140.
- [12] He C., Costeux S., Wood-Adams P., Delay J.M. (2003) Molecular Structure of High Melt Strength Polypropylene and its Application to Polymer Design. *Polymer*. 44: 7181-7188.
- [13] Muke S., Ivanov I., Kao N., Bhattacharya S.N. (2001) The Melt Extensibility of Polypropylene. *Polym. Int.* 50: 515-523.
- [14] Coccorullo I., Di Maio L., Montesano S., Incarnato L. (2009) Theoretical and Experimental Study of Foaming Process with Chain Extended Recycled PET. *eXPRESS Polymer Letters*. 3: 84-96.

- [15] Wagner M.H., Kheirandish S., Koyama K., Nishioka A., Minegishi A., Takahashi T. (2004) Modeling Strain Hardening of Polydisperse Polystyrene Melts by Molecular Stress Function Theory. *Rheol. Acta*. 44: 235-243.
- [16] Gendron R., Daigneault L.E., Caron L.M. (1999) Rheological Behavior of Mixtures of Polystyrene with HCFC 142b and HFC 134a. *J. Cell. Plast.* 35: 221-246.
- [17] Gendron R., Champagne M.F. (2004) Effect of Physical Foaming Agents on the Viscosity of Various Polyolefin Resins. *J. Cell. Plast.* 40: 131-143.
- [18] Champagne M.F. (2011) Foaming Polystyrene Using Blends of HFC: Solubility and Processing Behaviour. *Proceedings of 13<sup>th</sup> International Conference on Blowing Agents and Foaming Processes*. Düsseldorf. Paper 12.
- [19] Lee S.-T., Park C.B., Ramesh N.S. (2007) *Polymeric Foams: Science and Technology*. Boca Raton: CRC Press. 220 p.
- [20] Mihai M., Huneault M.A., Favis B.D. (2010) Rheology and Extrusion Foaming of Chain-Branched Poly(lactic acid). *Polym. Eng. Sci.* 50: 629-642.
- [21] Garancher J.P., Parker K., Shah S., Weat S., Fernyhough A. (2011) Industrial Trials of E-PLA Foams. *bioplastics MAGAZINE*. 6: 40-41.
- [22] Tai H. (2012) Batch Foaming of Amorphous Poly (DL-Lactic Acid) and Poly (Lactic Acid-co-Glycolic Acid) with Supercritical Carbon Dioxide: CO<sub>2</sub> Solubility, Intermolecular Interaction, Rheology and Morphology. In: De Vincente J., editor. *Rheology*. Rijeka: InTech. pp. 133-148. Available: [www.intechopen.com](http://www.intechopen.com).
- [23] Pilla S. (2011) Biodegradable PLA/PBAT Foams. *bioplastics MAGAZINE*. 6: 36-38.
- [24] Zhang J.-F., Sun X. (2007) Biodegradable Foams of Poly(lactic acid)/Starch. I. Extrusion Condition and Cellular Size Distribution. *J. Appl. Polym. Sci.* 106: 857-862.
- [25] Nabar Y., Narayan R., Schindler M. (2006) Twin-Screw Extrusion Production and Characterization of Starch Foam Products for Use in Cushioning and Insulation Applications. *Polym. Eng. Sci.* 46: 438-451.
- [26] Fang Q., Milford A.H. (2001) Preparation and Characterization of Biodegradable Copolyester-Starch based Foams. *Bioresource Technology*. 78: 115-122.
- [27] Schützenberger P. (1865) Action de l'acide acétique anhydre sur la cellulose, l'amidon, les sucres, la marmite et ses congénères, les glucosides et certaines matières colorantes végétales. *C. R. Acad. Sci.* 61: 485-486.
- [28] Edgar K.J. (2004) Cellulose Esters, Organic. Vol. 9. In: Mark H.F., editor. *Encyclopedia of Polymer Science and Technology*. Weinheim: Wiley-VCH. pp. 129-158.
- [29] Müller F., Leuschke C. (1992) Organische Celluloseester/Thermoplastische Formmassen. In: Bottenbruch L., editor. *Technische Thermoplaste: Polycarbonate, Polyacetale, Polyester, Celluloseester*. Munich: Hanser. pp. 396-457.
- [30] Zugenmaier P. (2004) Characteristics of Cellulose Acetates. In: Rustemeyer P., editor. *Macromolecular Symposia – Special Issue: Cellulose Acetates: Properties and Applications*. *Macromol. Symp.* 208: 81-166.
- [31] Mohanty A.K., Wibowo A., Misra M., Drzal L.T. (2003) Development of Renewable Resource-Based Cellulose Acetate Bioplastic: Effect of Process Engineering on the Performance of Cellulosic Plastics. *Polym. Eng. Sci.* 43: 1151-1161.

- [32] Zepnik S., Berdel K., Hildebrand T., Kabasci S., Radusch H.-J., van Lück F., Wodke T. (2011) Foam (Sheet) Extrusion of Externally Plasticized Cellulose Acetate. Proceedings of 13<sup>th</sup> International Conference on Blowing Agents and Foaming Processes. Düsseldorf. Paper 7.
- [33] Zepnik S., Berdel K., Hildebrand T., Kabasci S., Radusch H.-J., van Lück F., Wodke T. (2011) Influence of Physical Blowing Agent and Talc Content on the Foam Extrusion Behaviour and Foam Morphology of Externally Plasticized Cellulose Acetate. Proceedings of 3<sup>rd</sup> International Conference on Biofoams. Capri. pp. 262-270.
- [34] Zepnik S., Kabasci S., Radusch H.-J., Wodke T. (2012) Influence of External Plasticization on Rheological and Thermal Properties of Cellulose Acetate with Respect to Its Foamability, *J. Mater. Sci. Eng. A*. 2: 152-163.
- [35] Howell C.J., Trott D.W., Riley J.L. (1979) Process for Extruding Plasticized Open Cell Foamed Cellulose Acetate Filters. US Patent 4 180 536.
- [36] Mori H., Yoshida M., Matsui M., Nakanishi M. (2001) Biodegradable Cellulose Acetate Foam and Process for its Production. US Patent 6 221 924.
- [37] Jackson W.J., Darnell W.R. (1985) Process for Foaming Cellulose Acetate Rod. US Patent 4 507 256.
- [38] Redl A., Morel M.H., Bonicel J., Guilbert S., Vergnes B. (1999) Rheological Properties of Gluten Plasticized with Glycerol: Dependence on Temperature, Glycerol Content and Mixing Conditions. *Rheol. Acta*. 38: 311-320.
- [39] Liu D., Tian H., Zhang L. (2007) Influence of Different Amides as Plasticizer on the Properties of Soy Protein Plastics. *J. Appl. Polym. Sci.* 106: 130-137.
- [40] Wypych G. (2004) Handbook of Plasticizers. Toronto: ChemTec Publishing. 687 p.
- [41] Blasi P., Schoubben A., Giovagnoli S., Perioli L., Ricci M., Rossi C. (2010) Ketoprofen Poly(lactide-co-glycolide) Physical Interaction. *AAPS Pharm. Sci. Tech.* 8: E1-E8.
- [42] Guo J.-H. (1993) Effects of Plasticizers on Water Permeation and Mechanical Properties of Cellulose Acetate: Antiplasticization in Slightly Plasticized Polymer Film. *Drug Dev. Ind. Pharm.* 19: 1541-1555.
- [43] Hansen C.M. (2007) Hansen Solubility Parameters: A User's Handbook. Boca Raton: CRC Press. 544 p.
- [44] Barnes H.A. (2000) A Handbook of Elementary Rheology. Aberystwyth: Cambrian Printers. 210 p.
- [45] Spitael P., Macosko C.W. (2004) Strain Hardening in Polypropylenes and Its Role in Extrusion Foaming. *Polym. Eng. Sci.* 44: 2090-2100.
- [46] Cheng S., Phillips E. (2006) Rheological Studies on Radiation Modified Polyethylene Resins. Proceedings of Society of Plastics Engineers (SPE) ANTEC Conference. Charlotte.
- [47] Zwynenburg J. (2008) Predicting Polyolefin Foamability Using Melt Rheology. Available: <http://www.testplastic.com/pdfs/foams-2008-jim-zwynenburg.pdf>.
- [48] Bernnat A. (2001) Polymer Melt Rheology and the Rheotens Test. PhD Thesis. 119 p.
- [49] Koestner R.J., Mollon C.T., Schunk T.C., Gamble W.J. (2009) Method of Manufacture of a Polymeric Film with Anti-Blocking Properties. US Patent 7 597 956.



- [50] Okunev P.A., Dorofeev S.P., Nikolskii K.S., Kubaenko T.M., Kulikova E.S., Tsokolaev R.B. (1972) Gel-Penetrating Chromatography Method of Investigating the Influence of the Preparation Conditions on the Molecular Weight Distribution and Properties of Cellulose Acetate. *Fibre Chemistry*. 3: 166-168.
- [51] Minoshima W., White J.L., Spruiell J.E. (1980) Experimental Investigation of the Influence of Molecular Weight Distribution on the Rheological Properties of Polypropylene Melts. *Polym. Eng. Sci.* 20: 1166-1176.
- [52] Minegishi A., Nishioka A., Takahashi T., Masubuchi Y., Takimoto J.-I., Koyama K. (2001) Uniaxial Elongational Viscosity of PS/a Small Amount of UHMW-PS Blends. *Rheol. Acta*. 40: 329-338.
- [53] Muke S., Ivanov I., Kao N., Bhattacharya S.N. (2001) Extensional Rheology of Polypropylene Melts from the Rheotens Test. *J. Non-Newtonian Fluid Mech.* 101: 77-93.
- [54] Vachon C. (2005) Research on Alternative Blowing Agents. In: Gendron R., editor. *Thermoplastic Foam Processing: Principles and Development*. Boca Raton: CRC Press. pp. 152-204.
- [55] Kaewmesri W., Lee P.C., Park C.B., Pumchusak J. (2006) Effects of CO<sub>2</sub> and Talc Contents on Foaming Behavior of Recyclable High-melt-strength PP. *J. Cell. Plast.* 42: 405-427.
- [56] Pushpadass H.A., Babu G.S., Weber R.W., Milford H.A. (2008) Extrusion of Starch-based Loose-fill Packaging Foams: Effects of Temperature, Moisture and Talc on Physical Properties. *Packag. Technol. Sci.* 21: 171-183.
- [57] Micheali W., Schuhmacher H. (2006) The Effect of Talcum Particle Diameter on the Structure of PE Foam Sheets. *Proceedings of 8<sup>th</sup> International Conference on Blowing Agents and Foaming Processes*. Munich. Paper 13.
- [58] Jung U.P. (2007) Investigation of Foaming Behaviour of Thermoplastic Polyolefin (TPO) Blend. Bachelor Thesis. 40 p.
- [59] Heinz R. (2002) Prozessoptimierung bei der Extrusion thermoplastischer Schäume mit CO<sub>2</sub> als Treibmittel (Process Optimization for the Extrusion of Thermoplastic Foams Using CO<sub>2</sub> as a Blowing Agent). PhD Thesis. 120 p.
- [60] Naguib H.E., Park C.B., Lee P.C. (2003) Effect of Talc Content on the Volume Expansion Ratio of Extruded PP Foams. *J. Cell. Plast.* 39: 499-511.
- [61] Li G., Leung S.N., Wang J., Park C.B. (2006) Solubilities of Blowing Agent Blends. *Proceedings of AIChE Annual Meeting*. San Francisco. Paper # 75377.
- [62] Yao J., Berzegari M.R., Rodrigue D. (2010) Polyethylene Foams Produced Under a Temperature Gradient with Expancel and Blends Thereof. *Proceedings of 12<sup>th</sup> International Conference on Blowing Agents and Foaming Processes*. Cologne. Paper 17.
- [63] Ito Y., Yamashita M., Okamoto M. (2006) Foam Processing and Cellular Structure of Polycarbonate-Based Nanocomposites. *Macromol. Mater. Eng.* 291: 773-783.
- [64] Park C., Zhai W. (2010) Improving the Foaming Behaviour of Linear Polypropylene-Based TPO by Introducing Nanoclay. *Proceedings of 12<sup>th</sup> International Conference on Blowing Agents and Foaming Processes*. Cologne. Paper 16.