

The influence of additives on crystallization of blends based on polylactid acid

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Abstract. The sustainable development consists of the effort of replacing commonly used polymer materials for the biodegradable ones. They do not have sufficient physical and mechanical properties, therefore they have to be modified by producing various ratio mixtures or with the additives. Improving their processability and properties is an important challenge to be afforded before using these materials on the market. One way to improve the properties of these materials is to prepare their blends [1]. The most common way of the preparation of packaging materials is the injection moulding, where the crystallization of material is very important. That is the reason the crystallization has become one of the most studied characteristics of biodegradable blends based on PLA / PHB. The work is a contribution to works that deal with the description of the structure of PLA / PHB blends, which have been modified by the addition of various types of additives, mainly nucleating agents and plasticizers [2]. The films of these blends keep approximately unchanged mechanical properties after two weeks of storage. The presence of plasticizer (ATBC) and nucleating agent (BN) has no significant impact on the processing stability of PLA/PHB blends. The results show that the combination of the plasticizer and nucleating agent greatly affects the process of crystallization of PLA/PHB blends as well as the ratio of polymers and the heat treatment process.

1. Introduction

Nowadays, the most commonly used materials are polymers, both synthetic and natural. Their expansion is based on their good physical properties, mechanical properties, and also because of low production costs. The increasing consumption of conventional synthetic polymeric materials is the cause of the growing problem of their disposal. At the same time, we are faced with an ecological problem. For this reason, efforts are being made to replace conventional plastics (PE, PP, PS and others) with biodegradable plastics and therefore more environmentally friendly. One possibility how to solve this problem can be by the production of biodegradable plastics. Biodegradable polymers, especially those from renewable resources and their blends, are playing an important role in the field of research of new materials. Of all of the potential products made from annually renewable resources, polylactic acid (PLA) is currently the most interesting. This biopolymer is 100% renewable, it can be



easily composted and has comparable properties to commercially-known plastics [3,4]. The second group of studied polymers are polyhydroxyalkanoates, biopolymers synthesized by the action of microorganisms. As in the case of polylactic acid, these are polymers with similar properties to conventional plastics, they are completely biodegradable and have potential as a biodegradable substitute. The simplest and most commonly used poly- β -hydroxyalkanoate is poly- β -hydroxybutyrate (PHB) [5]. Polymers that are produced from natural resources and are capable of being decomposed in nature have worse physical and mechanical properties than conventional polymer materials and therefore, use of them in demanding applications and to replace conventional plastics, they have to be modified in some ways. One way to modify the properties of these materials is to prepare their blends. This method of the preparation can achieve a synergistic improvement in properties in the comparison with the pure components [6]. The properties of polymeric materials are generally improved during processing in accordance with the requirements of the final product application. One important factor for setting the processing conditions is the understanding and description of the polymer structure, which affects the final properties of the product. Based on the supramolecular structure, we can predict and control the resulting behaviour of polymeric materials [7]. Polymer blends are prepared as a result of improved processing and utility properties together with various additives and modifiers. The plasticizers are one of the most commonly applied additives to improve the processability and flexibility of the final product. Since the most common method of preparing polymeric materials is injection moulding where crystallization of the material is a very important factor, crystallization has become one of the most studied characteristics of PLA / PHB blends [8]. At the same time the crystallization is followed by the effect of other additives, nucleating agents on the crystallization process itself and their effect on the resulting mechanical properties. The present work is a contribution to the number of works dealing with the description of the crystalline structure of PLA / PHB blends which have been modified by the addition of various types of additives, mainly nucleating agents and plasticizers.

2. Materials

Polylactid acid $(C_3H_4O_2)_n$ – Ingeo 4043D, Mw = 202 kDa, PDI = 2,18 ; D-isomer content 4,2 %.
Nature Works, USA

Polyhydroxybutyrate $(C_4H_6O_2)_n$, Mw = 608 kDa, PDI = 4,23; homopolymer P3HB - Biomer,
Nemecko

Ester-type plasticizer – acetyltributylcitrate (ATBC), Jungbunzlauer, Nemecko (0, 5, 10, 15, 20,
25%wt.)

Nucleating agent – Boron Nitride (BN), Momentive, USA (BN – 0, 1, 5 % wt.)

3. Experimental

3.1 Blends preparation

Biodegradable blends based on PLA/PHB (60/40 w/w) with the specific content of additives were prepared using twin screw extruder (L/D = 40, D = 16 mm) at temperature 160 – 170 – 180 – 180 – 185 – 185 – 185 – 180 – 175 – 170 °C (direction hopper – head). Extruded materials were chilled in water and granulated into small pellets. Pellets were dried at 70°C for 2 hours in hot air oven and consequently used for rheological and DSC measurements.

3.2 Processing stability

The oscillation rheometer RPA 2000 was used for processing stability testing of prepared blends. Timed test was done at three temperatures: 170, 180, 190°C, the angle of strain was 30° and oscillation frequency was 60 cpm. For correct evaluation of temperature influence on the rate of polymer degradation based on the decrease of complex viscosity, the elimination of differences in initial viscosity was done by recalculation of complex viscosity using the formula (1):

$$\eta_{rel}^*(t) = \eta^*(t) / \eta^* \quad (1)$$

where $\eta_{rel}^*(t)$ is relative complex viscosity at time t , $\eta^*(t)$ is complex viscosity at time t and η^* is complex viscosity at the start of the test.

3.3 Films preparation

For films preparation was used single-screw Brabender extruder (screw diameter 19 mm, L/D=25) as well as chill-roll technology was used. Prepared films were used for measuring the mechanical properties. The selected temperature profile of the single screw extruder in the head \rightarrow hopper direction was as follows: 170-180-180-170 °C.

3.4 Mechanical properties measurement

Tensile strength at break (σ_b) and the elongation at break (ϵ_b) were determined according to ISO 527 standard using Zwick machine at cross-head speed 50 mm/min. Strips 15mm width were used as testing pieces.

3.5 DSC measurement

DSC (Mettler Toledo) was used for studying the crystallization properties of prepared blends under specific conditions. The flow of purge gas of nitrogen was 50ml/min. Standard aluminium crucibles were used. Measuring program:

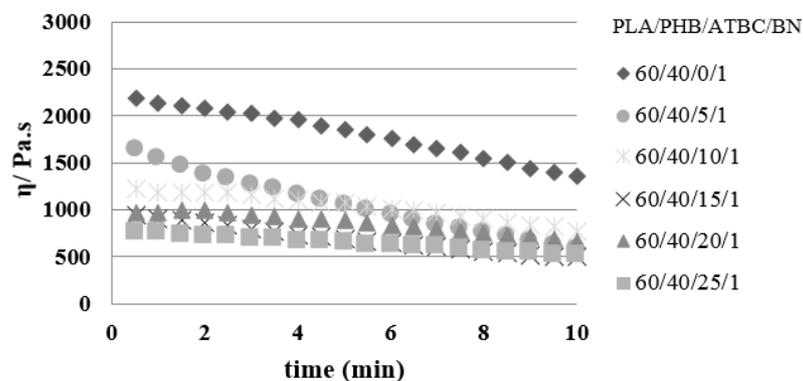
1. Heating 10 K/min, 30-190 °C
2. Isothermal process 190 °C, 3 min
3. Cooling 10 K/min, 190-30 °C
4. Isothermal process 30 °C, 3 min
5. Heating 10 K/min, 30-190 °C

4. Results and discussion

The work deals with the study of influence of plasticizer and nucleating agent on crystallization process and the resulting thermal and physical properties of PLA/PHB blends.

4.1 Processing stability

The indication of the first stages of degradation process of polymers can be easily detected using the oscillation rheometer. Changes in relative complex viscosity of the prepared blends were taken as the indicator of processing stability. According to article [9], it was shown that changes in relative complex viscosity reflect changes in molecular weight of degraded polymer very well. The example of dependency of complex viscosity and relative complex viscosity on test time for PLA/PHB blends including 1% wt. of nucleating agent and different concentration of plasticizer is shown in Figure 1.



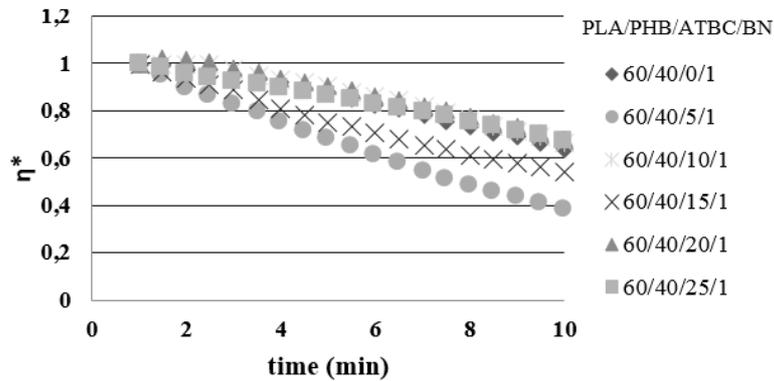


Figure 1. The dependency of complex viscosity and relative complex viscosity on test time for PLA/PHB blends including 1% wt. of nucleating agent and different concentration of plasticizer

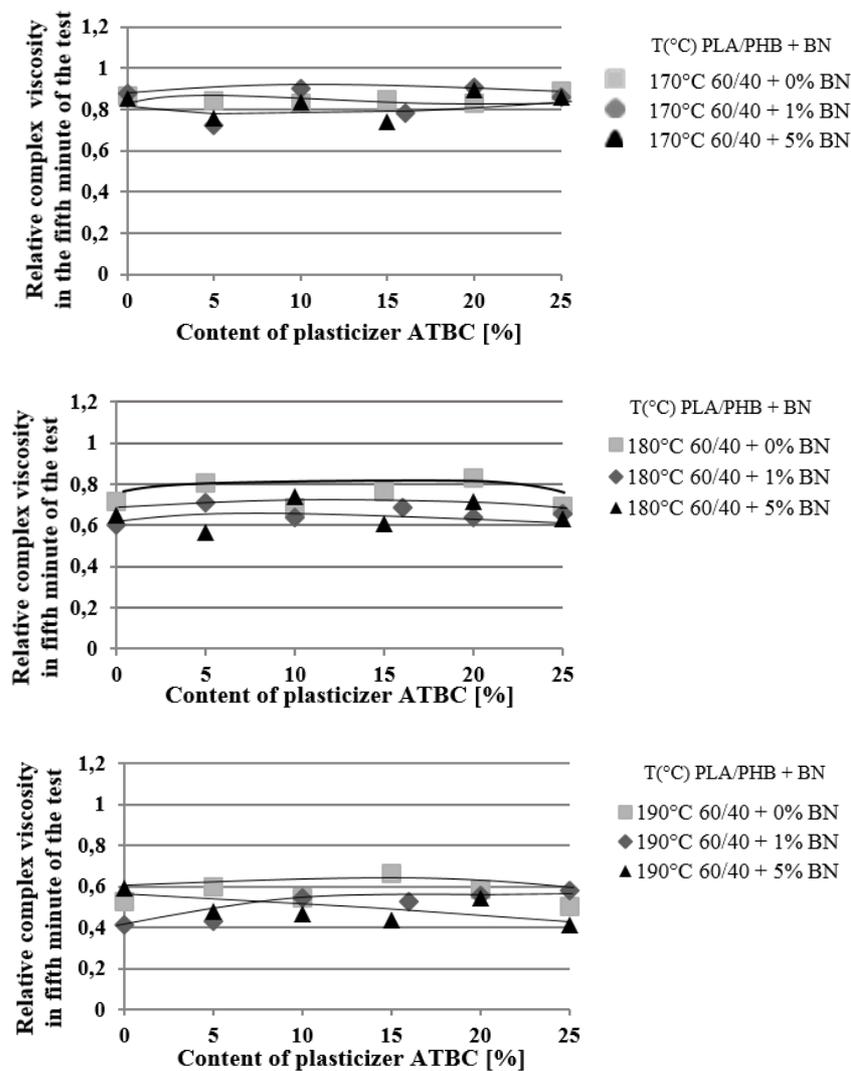


Figure 2. The dependency of relative complex viscosity in the fifth minute of the test on content of plasticizer and nucleating agent BN at different temperatures (170 °C, 180 °C, 190 °C).

According to results shown in Figure 2 it can be seen that the viscosity of the blends in the fifth minute of the test, because of the thermo-mechanical stress caused by oscillatory rheometer, gradually decreases with temperature and it indicates that the increasing temperature causes the expected increase of degradation of the polymer blends. Differences in relative complex viscosity are significant but slightly. The effect of the presence of the nucleating agent, as well as the influence of the concentration of plasticizer is minimal and the observed differences can be considered to be within the experimental variability. Consequently, neither the plasticizer nor the nucleating agent has a negative effect on the processing stability or rheological characteristics of the studied blends.

4.2 Mechanical properties

The PLA / PHB blends were prepared according to method mentioned in chapter 3.1. Subsequently, the physical-mechanical properties of PLA / PHB blends were measured according to method mentioned in chapter 3.4 after sample preparation at time intervals 24 hours, a week and 2 weeks after the extrusion. The conditions for storage of samples were 50% relative humidity and 25°C. Nucleating agent BN is also used as a filler in high performance in polymer blends, which greatly improves thermal conductivity. In film production, this property of BN appears to have been evident. The addition of a larger amount of BN (5 wt.%) has a positive effect on the processing properties either during the production of the pellets or the film, probably due to the better thermal conductivity of the prepared blends. Whether cooling in a water bath or cooling on chill rolls, it is likely that a faster heat transfer occurs, resulting in the stiffness of string and a reduced stickiness of the films on the chill rolls. For all samples (PLA/PHB : 60/40 w/w ratio), physical-mechanical properties were maintained after 2 weeks of storage. For this reason, in the following, we only summarize the PLA / PHB blends, depending on the different plasticizer and nucleating agent content after 2 weeks of storage. The elongation at break for 60/40 w/w PLA / PHB blends (Figure 3) with 0, 1 and 5 wt.% of nucleating agent is noted after the addition of 15 %wt. of the plasticizer, and above this plasticizer concentration no change are observed in the elongation with the increase amount of the plasticizer. The addition of the nucleating agent does not affect the elongation at break and value of ϵ_b can to be considered as similar except the highest concentration of both additives when the elongation at break is slightly lower.

The tensile strength at break (Figure 4) decreases with the addition of 0-15% of plasticizer, the most significant decreasing can be observed in the range of 10-15%, from 15% of plasticizer we do not notice a significant change in tensile strength at break. The differences in tensile strength at break caused by presence of nucleating agent are more significant in case of low concentration of plasticizer to compare with differences at higher concentration of plasticizer, which are very small.

Based on described mechanical properties of prepared blends the marginal effect of presence of nucleating agent was observed in case of both tensile parameters. More significant effect was noticed in the case of presence of plasticizer as additive in different concentrations.

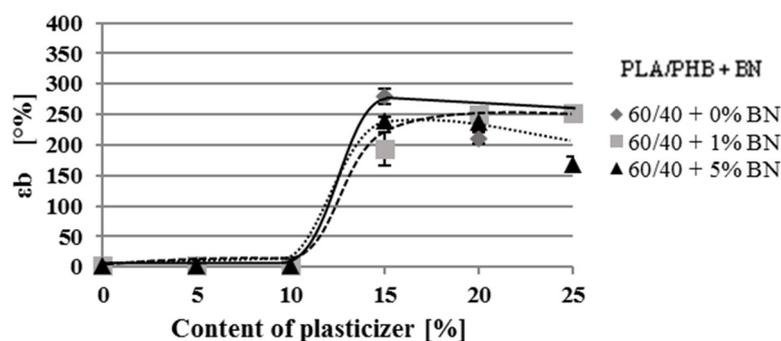


Figure 3. The dependency of elongation at break on content of plasticizer after two weeks of storage.

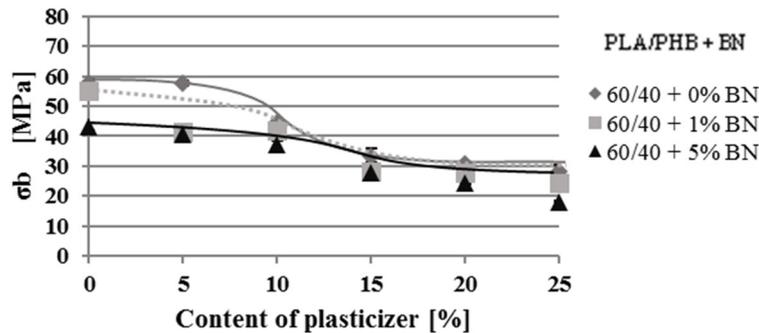


Figure 4. The dependency of tensile strength at break on content of plasticizer after two weeks of storage.

4.3 Thermal properties

The thermal properties of prepared blends were studied by DSC, especially the crystallization process. It is well known that the first heating curve is significantly influenced by the sample's thermal history. The thermal history of prepared samples was erased by first heating run which is not reported because it reflects more thermal history of the sample preparation than real material characteristics. Only cooling and the second heating curves are presented in Figure 5 and Figure 7. The curves of cooling are shown in Figure 5, dependency of crystallization temperature T_c (peak) on nucleation agent as well as plasticizer concentration is shown in Figure 6. It can be seen that the addition of nucleating agent significantly influences the crystallization of PLA/PHB blends. The crystallization peak is shifted to a higher temperature in comparison to blank PLA/PHB blend. The changes of T_c depend also on plasticizer concentration. With increasing content of plasticizer, crystallization peak of nucleated blends is shifted to lower temperature. It means, that during the cooling of the melt, the crystallization process starts earlier as an effect of nucleation agent and it starts later as an effect of plasticizer, probably because plasticizer allows better mobility of the polymer chains. It can be predicted that the presence of other types of plasticizers can exhibit more or less strong effect on crystallization process of PLA/PHB blends in presence of nucleating agent in dependency of interaction between plasticizers and polymers. It means that by suitable selection of nucleation agent and plasticizer as additive in combination, the temperature of crystallization can be modified.

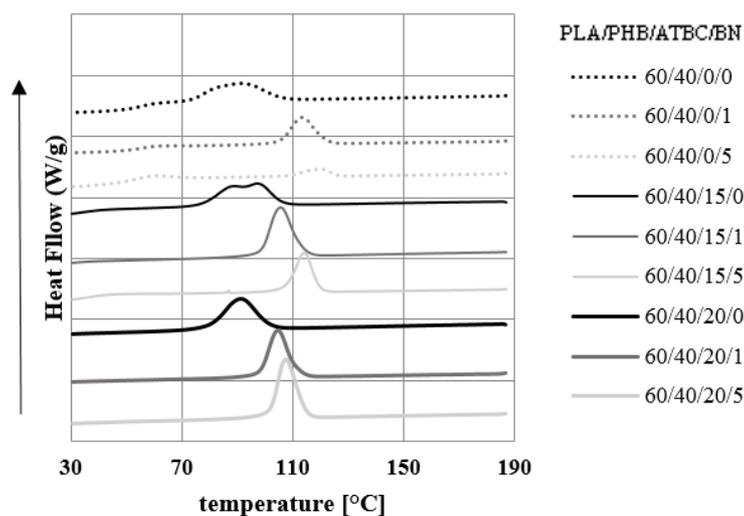


Figure 5 The curves of cooling of prepared blends. Ratio: PLA/PHB/plasticizer/nucleating agent.

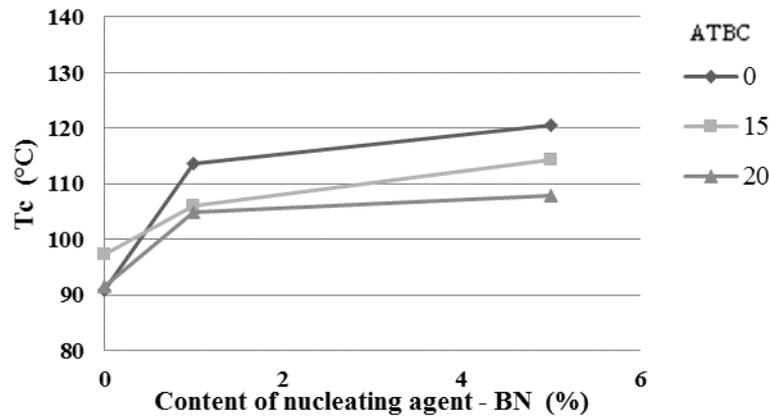


Figure 6 The dependency of Tc on nucleation agent content for various concentration level of plasticizer.

The curves of the second heating are shown in Figure 7, where three processes can be observed - the cold crystallisation, the melting of PLA and the melting of PHB. The effect of cold crystallization is present due to low rate of crystallization of PLA during cooling of samples. The dependency of Tcc as the peak value on both additives concentration is shown in Figure 8. The difference in nucleating activity is observed according to presence of nucleating agent as well as plasticizer. The Tcc of cold crystallization is shifted to higher temperature with increasing content of nucleating agent, mainly if blend contains no plasticizer. On the other hand, the increasing content of plasticizer shifts Tcc to lower temperature. This effect allows to modify crystallization process via the processing condition during the processing (temperature of the mould, in injection moulding process for example). Figure 9 shows the dependencies of Tm for PLA as well as for PHB on both additives concentration. Both melting temperatures (for PLA and PHB polymers in the blend) are strongly shifted to lower values by plasticizer concentration. The activity of nucleating agent is influenced by plasticizer as well. It can be seen, based on DSC results, that the crystallization of the blends and the type of crystals formed can be significantly influenced by the influence of the additives.

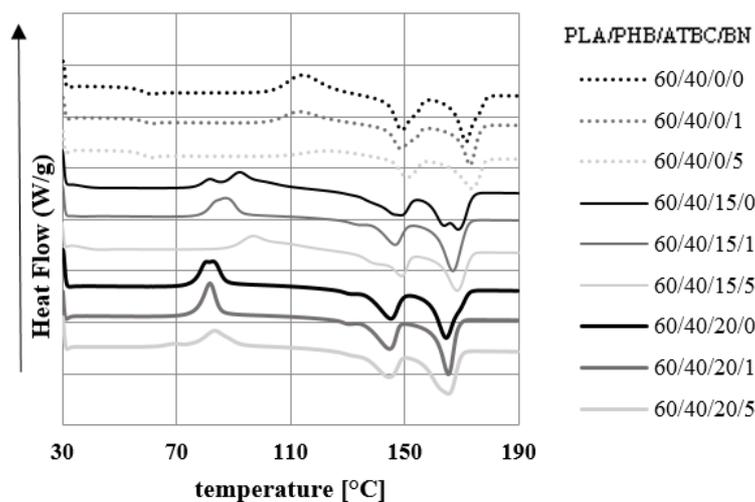


Figure 7. The curves of the second heating of prepared blends. Ratio: PLA/PHB/plasticizer/nucleating agent.

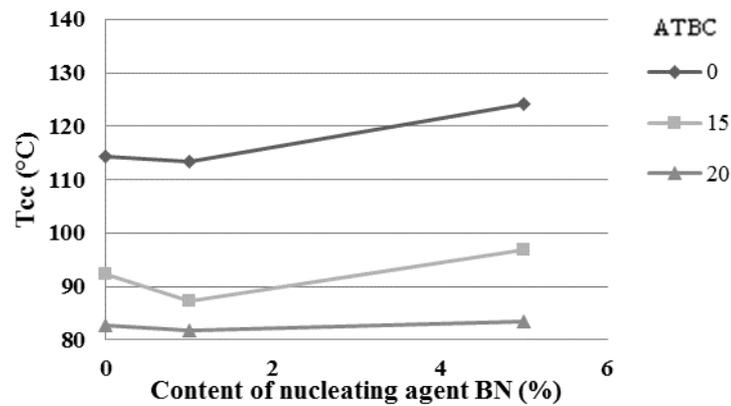


Figure 8. The dependency of T_{cc} on nucleating agent concentration for various levels of plasticizer content.

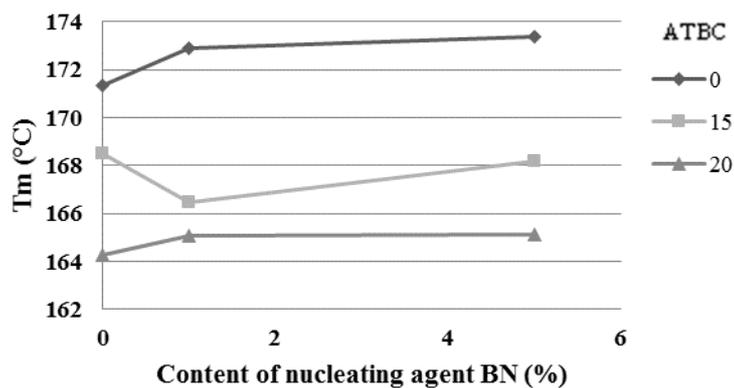
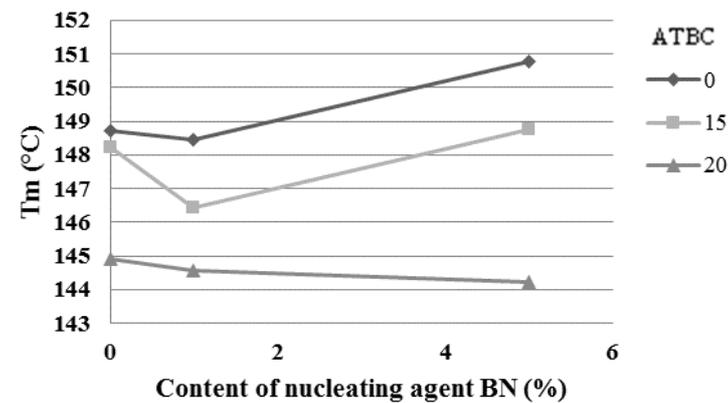


Figure 9. The dependency of T_m on nucleating agent concentration for various levels of plasticizer content.

Polymorphism, but also the process of cold crystallization and melting, is significantly affected. Generally, the nucleating agent (BN) increases the rate of crystallization process of PLA / PHB blends and the plasticizer improves the mobility of the segments to shift the temperature of melting and cold crystallization to lower temperature during the heating of the blend.

5. Conclusion

Neither the plasticizer nor the presence of a nucleating agent has significant impact on the processing stability of PLA / PHB blends. The addition of the nucleating agent has negative impact on the physical-mechanical properties of prepared blends as compared to blends without nucleating agent, especially in the case of tensile strength at break (σ_b) which decreases compared to samples without nucleating agent. The elongation at break significantly improves over 10% of plasticizer content. Additives, in our case nucleating agent and plasticizer, affect the crystallization process. In general, the nucleating agent (BN) improves nucleating activity of PLA/PHB blends and plasticizer allows better mobility of the chains that results in lower crystallization temperature. The next study will be based on optimizing the composition and processing conditions of PLA/PHB blends.

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