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STUDY ON EFFICIENCY OF SOLID-STATE POLYCONDENSATION ON POLY(ETHYLENE TEREPHTHALATE)/CARBON NANOTUBE COMPOSITES

One of the problems concerning carbon nanotube (CNT)/thermoplastic polyester composites, prepared by *in situ* synthesis, is usually a lower molecular weight of the polymer matrix when compared to a homopolymer polymerized in the same conditions. It results in lower elongation at break/mechanical strength of the polymer, which may diminish the reinforcing effect coming from polymer/CNT interactions in the composite. Extension of the reaction time brings, in turn, problems with extruding the melted composite from the reactor due to its high viscosity and in consequence material waste. The objective of this study was to evaluate the efficiency of the solid-state polycondensation process (SSP), which is commonly applied to thermoplastic polyesters on an industrial scale, as regards poly(ethylene terephthalate) (PET) filled with single-walled (SWCNT) or multi-walled (MWCNT) carbon nanotubes. The experiments were carried out using a laboratory-made vacuum SSP set-up. The presented results prove the relatively high efficiency of the process, however, the material geometry seems to be a key factor. The best results were achieved for samples with the smallest thickness. Moreover the presence of nanoparticles in the polymer does not prevent or hinder further polymerization in the solid, and the reaction effectiveness is even higher in CNT composites when compared to an unfilled polymer.

Keywords: carbon nanotubes, polymer composites, *in situ* synthesis, solid-state polycondensation

OCENA EFEKTYWNOŚCI PROCESU DOPOLIKONDENSOWANIA W STANIE STAŁYM KOMPOZYTÓW NA BAZIE POLI(TEREFTALANU ETYLENU) Z UDZIAŁEM NANORUREK WĘGLOWYCH

Jednym z problemów w pracach badawczych nad wytwarzaniem kompozytów poliestrowych z udziałem nanorurek węglowych (CNT) metodą syntezy *in situ* jest trudność w uzyskaniu odpowiedniej masy cząsteczkowej osnowy polimerowej w porównaniu z masą poliestru syntezowanego w tych samych warunkach, lecz bez udziału nanonapełniaczy. Może to niwelować spodziewany efekt wzmocnienia, wynikający z oddziaływań polimer-nanonapełniacz. Wydłużenie zaś syntezy kompozytu wiąże się z trudnościami z wytłoczeniem materiału z reaktora na skutek jego dużej lepkości i stratami materiału. Celem prezentowanych badań było zbadanie efektywności procesu polimeryzacji w stanie stałym (SSP), jaki stosuje się w warunkach przemysłowych m.in. do termoplastycznych poliestrów, w zastosowaniu do kompozytów poli(tereftalanu etylenu) z udziałem jedno- i wielościennych nanorurek węglowych. Eksperymenty prowadzono na próbkach o różnej geometrii, tj. granulacie, elementach wyprasek oraz cienkich foliach. Wyniki badań w skali laboratoryjnej wskazują na stosunkowo wysoką efektywność dopolikondensowania, przy czym zarówno w przypadku homopolimeru, jak i kompozytów największy przyrost mas cząsteczkowych uzyskano dla materiałów w postaci folii. Ponadto potwierdzono, iż obecność nanostruktur nie tylko nie stanowi ograniczenia dla reakcji polimeryzacji w stanie stałym, ale również efektywność procesu w przypadku kompozytów jest większa niż dla polimeru bez udziału CNT.

Słowa kluczowe: nanorurki węglowe, kompozyty polimerowe, synteza *in situ*, proces dopolikondensowania

INTRODUCTION

Polymer composites containing carbon nanomaterials are receiving special attention from both research and business groups due to their high application perspectives. Particular interest is focused on composites/nanocomposites filled with carbon nanotubes (CNTs), as their very high aspect ratio along with extremely high mechanical strength predominate the advantages of graphene nanoplatelets in preparing structural composites [1-4]. What is also important, the permanent development of CNT synthesis methods results in a gradual decrease in prices, which allows for composites production on a mass scale [5].

Among polymer/CNT composites preparation methods, *in situ* polymerization is broadly investigated in applications for both reactive and thermoplastic polymers, including thermoplastic polyesters. The idea of this method is to introduce nanoparticles into the polymer during its chemical synthesis, and the obtained composites can then be processed and characterized to reflect the real properties of a potential final product

[6, 7]. The synthesis is preceded by dispersing the nanotubes in a liquid substrate to ensure homogeneous CNT distribution in the composite. The disadvantage of this method is observably a lower molecular weight of the polymer matrix when compared to the molecular weight of a homopolymer synthesized under the same conditions [8-11]. It is because of the increase in viscosity of the reaction mixture by the presence of nanotubes with a very large specific surface area and restricted mobility of the growing polymer chains. In consequence polymerization slows down. Extension of the reaction time is not a solution, as it brings problems with extruding the composite from the reactor due to the thixotropic-like behaviour of CNTs on polymer melt. It is recognized by a significant increase in melt viscosity under relatively low shear stress that prevents the composite from flowing down to the reactor bottom. All these inconveniences result in an insufficiently high molecular weight of the polymer matrix, thus lower elongation at break/mechanical strength, which in turn may diminish the reinforcing effect coming from polymer/CNT interactions.

In order to improve the molecular weight of the polymers, the solid-state polycondensation (SSP) could be applied [12, 13]. It is the next step after polymerization in a molten state. The idea is to heat the material of a relatively small molecular mass to a temperature higher than glass transition (Tg), but only slightly lower than the melting point (Tm) under reduced pressure. The applied conditions initiate the diffusion of polymer chain end groups to react to one another, but the reaction by-products must be removed from the solid to continue the reactions in the whole volume of material. It shifts the process equilibrium towards an increase in molecular weight. SSP efficiency is determined not only by the estrification reactions, diffusion of by-products through the solid and their evaporation from the sample surface, but also by the geometry of the material pieces (i.e. their specific surface area), process temperature and duration, polymer crystallinity degree, and the manner of by-product removal for the reaction environment [14-16]. The post-polycondensation process is commonly used in industry for thermoplastic polyesters produced in a batch (periodic) system. For instance, it is applied to commercially synthesized poly(ethylene terephthalate) (PET), when a higher molecular weight is desired for some applications (e.g. bottle or fibre production) [13]. In this study, the presented results prove that solid-state polycondensation could be also applied to PET composites containing single- or multi-walled carbon nanotubes.

EXPERIMENTAL PROCEDURE

Synthesis of PET/CNT composites

The SSP process was carried out on poly(ethylene terephthalate) based composites containing 0.1 wt.% single-walled (SWCNT, CNI Technology Co., USA)

and multi-walled (MWCNT; Nanocyl S.A., Belgium) carbon nanotubes. The polymer composites were obtained in situ in two-stage polycondensation in a molten state. Appropriate amounts of dimethyl terephthalate (DMT), ethylene glycol (EG) and catalysts (zinc acetate and antimony(III) oxide) were placed in a 1 dm^3 - capacity steel reactor (Autoclave Engineers Pennsylvania, USA) equipped with horse-shoe stirrer. The synthesis was preceded by dispergation of the carbon nanotubes in EG to break up the existing agglomerates and ensure their uniform distribution in the polymer matrix. A detailed procedure of the composite synthesis is presented elsewhere [8, 11, 17, 18]. When the polycondensation was completed, the composites in a molten state were extruded from the reactor into a cooling bath and granulated.

Solid-state polycondensation of materials

In industrial SSP reactors there are two methods to remove reaction by-products during the process: by passing nitrogen through the reacting mass or by maintaining a reduced pressure [13]. The first solution is more common, because the inert gas flowing countercurrently up through the polymer deposit eliminates the temperature gradient and helps both by-products and moisture to evaporate. However, applying a dynamic vacuum-pumping process has also found to be effective and this solution has been used in our laboratory set-up. The scheme of the set-up is presented in Figure 1. Before the SSP process, ca. 20 g of homopolymer and composite samples in the form of platelets, chips or thin films were placed in the autoclave in aluminium pans separated from the autoclave bottom by PTFE roundels. The process temperature was determined according to DSC thermographs (TA Instruments Q100) of the CNT/polymer composites, whilst the process duration was set experimentally. The post-polycondensation effectiveness was evaluated upon changes in intrinsic viscosity [η] and viscosity-average molecular weight M_v of the composite matrix as regards variable process conditions.
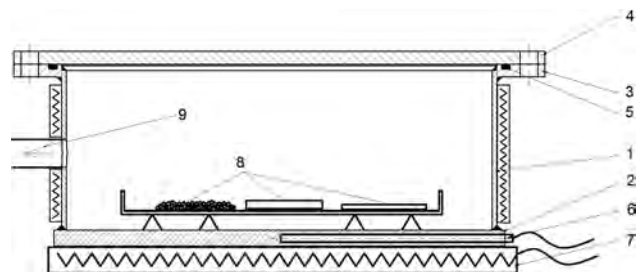

Fig. 1. Vacuum solid-state polycondensation set-up: 1 - autoclave, 2 - bottom wall, 3 - flange, 4 - lid, 5 - o-ring seal, 6 - thermocouple, 7 - heating elements on autoclave bottom and circumference, 8 - SSP treated materials, 9 - outlet for vaccumm pump and by-products

Rys. 1. Autoklaw do polikondensacji w stanie stałym pod obniżonym ciśnieniem: 1 - ścianka, 2 - dno, 3 - kołnierz, 4 - pokrywa, 5 - uszczelnie „o-ring", 6 - termopara, 7 - elementy grzewcze na dnie i obwodzie autoklawu, 8 - próbki poddawane procesowi dopolikondensowania, 9 - odprowadzenie do pompy próżniowej i produktów ubocznych

Testing methodology

Material samples in the shape of virgin platelets as well as after processing: crumbled injection-moulded elements, called "chips", and thin films have been used in this study. The injection-moulded elements were processed at 270°C under a pressure of 70 MPa, and then cut into regular pieces or used for compression moulding in order to prepare thin films. The compression temperature was 265°C and pressure 10 MPa. Before thermal processing, all the granulates were dried at 80°C within 5 h under reduced pressure in order to remove moisture. The approximate dimensions of the samples were as follows: for the platelets ca. 1.5 mm in diameter and 7 mm in length, for the chips 5 x 6 mm and 2 mm in thickness, for the films 10 x 10 mm with a thickness of ca. 100 μm for unfilled PET and 150÷250 μm for PET/CNT composites.

The intrinsic viscosity [η] before and after the SSP proces was measured using an Ubbelohde viscometer at 35°C in a mixture of phenol/ 1,1,2,2-tetrachloroethane (60/40 wt.%). The polymer solutions had a concentration of 0.5 g/dl, and after dissolving they were filtered to separate the CNTs and their agglomerates. Filtration was also applied to the homopolymer solution. Viscosity-average molecular weight M_v was determined using the Mark-Houvink equation for solutions with very low concentration: $[\eta] = K \cdot M_v^{\alpha}$, where $K = 125 \times 10^{-5}$ dl/g and $\alpha = 0.65$ [19]. The efficiency of solid-state polycondensation was calculated as the percentage increase in the average molecular weight after a specified SSP duration related to the molecular weight of the polymer prior to SSP.

RESULTS AND DISCUSSION

As mentioned in the Introduction, lower molecular weights of the polymer matrix when compared to a homopolymer polymerized in the same conditions, result in the presence of nanoparticles, which restrict the mobility of growing polymer chains. Furthermore, although *in situ* synthesis of the composites is continued up to reaching the same level of viscosity as the homopolymer, measured by the stirrer torque, the molecular weight of the matrix is lower. The post-polycondensation process seems to be a solution to this problem, however, the study findings have indicated that not only the temperature and duration, but also the geometry of the material pieces were the key factors.

According to the DSC thermographs (Fig. 2), the melting of the smallest crystallites in both unfilled PET and PET-based composites starts at the temperature range of 208÷210°C, and the endotherm maximum is observed at ca. 245°C. In order to ensure high macromolecular mobility, but at the same time to avoid sticking of the polymer pieces and diminishing the surface area for by-product diffusion, the temperature of 235°C was determined for SSP. The process duration was set based on experiments for unfilled PET in the form of platelets.
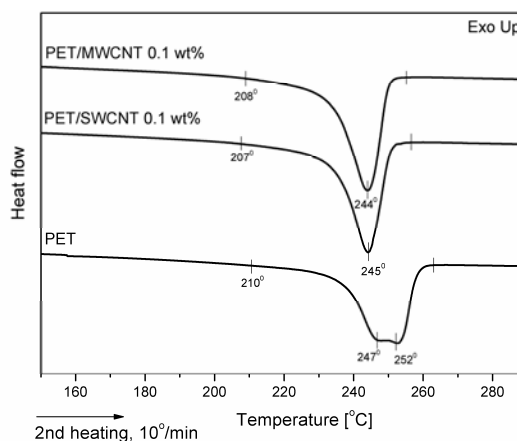

Fig. 2. DSC thermographs for PET, PET/SWCNT, and PET/MWCNT
Rys. 2. Termogramy DSC dla PET, PET/SWCNT i PET/MWCNT

Presented in Table 1, the values of PET molecular mass for various samples after a specified time of SSP, clearly indicate the differences determined by the material form. In the case of fine platelets, the molecular weight vividly changes along with the process duration. Within the first hour, some unfavourable reactions, like very fast depolymerisation or hydrolytic degradation in the presence of moisture and higher temperature, may take place. It results in a rapid molecular weight drop. However, along with time those destructive reactions give way to gradual growing of the macromolecules, and a progressive increase in the intrinsic viscosity after the second and every next hour is observed. Finally, the SSP efficiency for platelets reached ca. 80% after 5 hours of process duration, which is a moderate result when referred to literature data, e.g. Ma et al. [15] reported a few times higher increment in [η]. Better results were achieved for the samples in the form of films - the molecular weight of the homopolymer increased almost twice, and in the case of the composites even more than twice (Table 2). However, the highest efficiency of the process is observed within the first 2 hours, in the next two the increase is relatively lower (Fig. 3). It is a practically important finding, as when the level of intrinsic viscosity achieved after 2 h is suitable for a particular application/product, there is no need to extend the post-polycondensation process. Moreover the comparison of the results obtained for platelets and thin films proves that the geometry in which all the dimensions are very close as in the case of fine granulates, results in a longer way for the by-product to diffuse and a relatively small transfer area. The sample geometry, in which two dimensions (surface area) are much larger than the third one (thickness), is more favourable because it minimizes the temperature gradient within the material, reduces the way of glycol evacuation as well as increases the solid surface for glycol to evaporate. All these factors drive the polymerization forward. Indeed, materials in the form of chips, which were characterized by the largest dimensions, as well as thickness, show the lowest efficiency in intrinsic viscosity increment. It is also worth

noting that the thermal history of the treated material does not affect considerably SSP effectiveness, though the molecular weights for the films and chips determined before the process were slightly lower than the molecular weights for the virgin granulate.

TABLE 1. **Values of intrinsic viscosities and viscosity–average molecular weights for PET after various SSP durations**

TABELA 1. **Wartości GLL i średnich mas cząsteczkowych dla próbek PET po różnych czasach dopolikondensowania**

[η], dl/g M_v	Unfilled PET					
	before SSP	after 1 h SSP	after 2 h SSP	after 3 h SSP	after 4 h SSP	after 5 h SSP
Platelets	0.49 9 800	0.36 6 100	0.58 12 700	0.61 13 700	0.68 16100	0.71 17 300
Films	0.47 9 200	-	0.71 17 300	-	0.77 19 600	-
Chips	0.47 9 200	-	0.55 11 700	-	0.61 13 700	-

TABLE 2. **Values of intrinsic viscosity and viscosity-average molecular weights for PET/CNT composite after various SSP durations**

TABELA 2. **Wartości GLL i średnich mas cząsteczkowych dla kompozytów po różnych czasach dopolikondensowania**

[η], dl/g M_v	PET / SWCNT			PET / MWCNT		
	before SSP	after 2 h SSP	after 4 h SSP	before SSP	after 2 h SSP	after 4 h SSP
Platelets	0.44 8 300	0.68 16 200	0.74 18 400	0.47 9 200	0.67 15 800	0.75 18 800
Films	0.44 8 300	0.75 18 800	0.78 19 900	0.46 8 900	0.73 18 000	0.77 19 600
Chips	0.43 8 000	0.64 14 700	0.70 16 900	0.46 8 900	0.65 15 100	0.72 17 600

As mentioned before, an improvement in molecular weight by the post-polycondensation process was observed for both the homopolymer and PET/CNT composites, however, interestingly a much higher efficiency was achieved for the composites. It seems that the presence of nanoparticles exhibiting much a higher stiffness and larger sizes as compared to macromolecules, might considerably restrict the mobility of the reacting polymer chain ends, therefore diminishing polymerization effectiveness. In fact, the nanotubes distributed in the polymer facilitate glycol diffusion due to the relatively weak adhesion in the polymer/CNT interfaces. Actually, it is well known that carbon nanotubes are naturally incompatible with polymers, and in order to strengthen the common interactions, surface functionalization of CNT is applied. Neither SWCNT nor MWCNT used in this study were subjected to chemical modification, and the composite sample fractures reveal free CNT ends pulled out from the polymer during fracturing (Figs. 3 and 4).

It confirms the rather weak adhesion between the composite phases. Thus it can be assumed, that in the case of the investigated composites, the interfaces make free spaces for by-product molecules to exit the polymer mass. What is more, when the nanotubes are uniformly distributed, this free volume further facilitates the evacuation of glycol, which drives the polymerization and its efficiency. The better effects achieved for SWCNT - containing composites may be explained by the higher specific surface area of the nanotubes as compared to MWCNT, which provides an even larger area of molecule diffusion. The presented studies confirmed indeed that the presence of nanoparticles in the polymer does not prevent or hinder further polymerization in the solid, and a post-polycondensation process can be applied to *in situ* composites with success, but also the reaction effectiveness is even higher in CNT composites when compared to an unfilled polymer.
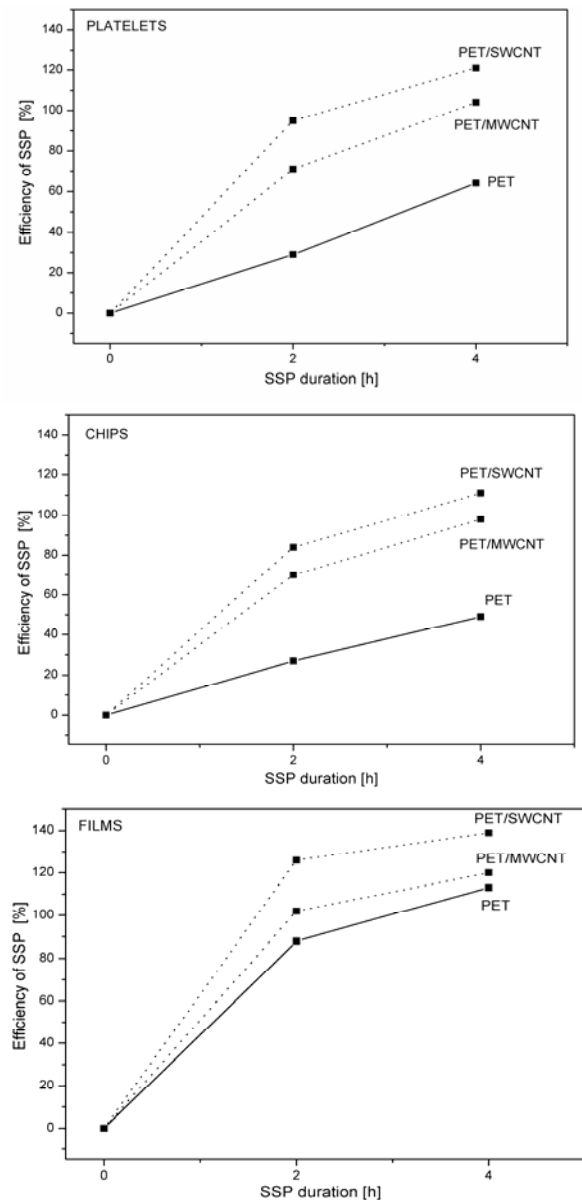

Fig. 3. Efficiency of SSP process depending on material form

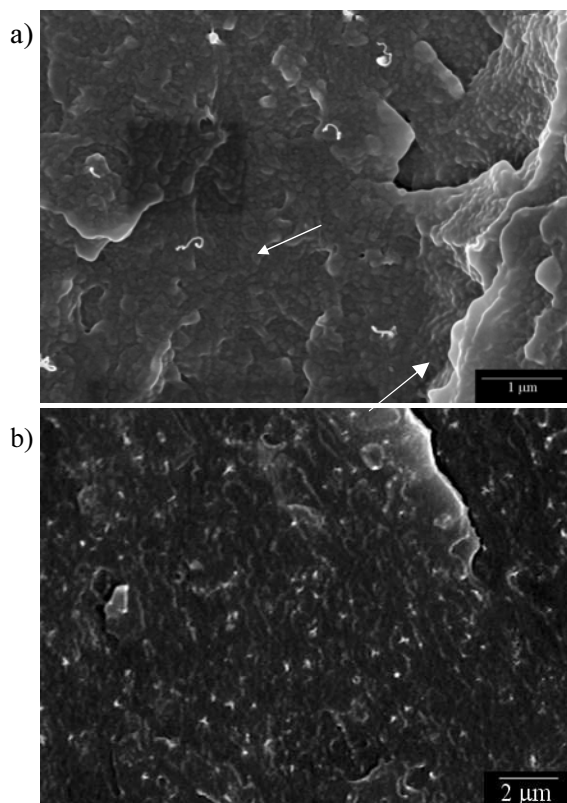Rys. 3. Efektywność procesu dopolikondensowania zależnie od postaci materiału

Fig. 4. SEM micrographs of PET composites containing 0.1 wt.%
a) SWCNT, b) MWCNT

Rys. 4. Mikrografie SEM kompozytów PET zawierających 0,1% wag.
nanorurek węglowych: a) SWCNT, b) MWCNT

CONCLUSIONS

The presented results prove that solid-state poly-condensation may successfully be applied to carbon nanotubes containing composites based on thermoplastic polyesters, wherein the key factor is the geometry of the material subjected to the process. The larger the surface area and smaller thickness, the more efficient glycol diffusion from the mass, which drives the reactions between the polymer chains. The advantage coming from SSP is not only an increase in the molecular weight of the polymer matrix, but also avoiding inconveniences associated with an extension of the *in situ* synthesis of the composites, particularly problems with composite extrusion from the reactor. However, when analyzing the obtained results one should keep in mind that all the experiments were realized on laboratory scale, for relatively small quantities of materials. When scaling up, there might be a problem with ensuring a specified material geometry (e.g. thin films) because in the case of platelets/granulate, the SSP process seemed to be moderately effective.

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