IDŐKÖZI BESZÁMOLÓ **szakmai beszámoló**				NKFI-azonosító: 138430	Típus: PD
				Szakmai jelentés: 2022. 10. 27	
Vezető kutató: Polyák Péter		Kutatóhely: Fizikai Kémia és Anyagtudományi Tanszék (Budapesti Műszaki és Gazdaságtudományi Egyetem)			
Zsűri: KM2	Kezdet: 2021. 10. 01	Időszak: 2021-10-01 - 2022-09-30	Főkönyviszám: 71203	Nyomtatás: 2023. 07. 14.	

Pályázat címe:	Poliolefinek helyettesítése mikrobiális poliészterekkel
A kutatási projektben résztvevő kutatók azonosak a szerződésben szereplő kutatókkal? (Amennyiben nem azonosak, akkor kérjük, hogy az NKFI Hivatalnak címzett, elektronikusan benyújtott kérelemben jelezze a változást. A kutató résztvevőket csatlakoztatni szükséges a projekthez az EPR-ben.)	igen
Az elvégzett munka megfelel-e a munkatervben tervezettnek?	igen

Az elért eredmények rövid ismertetése:

The goal of the project OTKA PD 138430 is the substitution of polyolefins with microbial polyesters. Although polyolefins are applied in many fields, these areas can still be sorted into two very distinct categories.

The first category comprises applications and products of a high added value, such as accessories for the medical and pharmaceutical industries. These products are generally of a considerable cost, and the methodology of their production is based on many versatile technologies. Conversely, the products that belong to the second category, i.e., packaging, generally represent a marginal added value. Their manufacturing is carried out by using a rather limited amount of (conventional) technologies. Among these conventional, high-output, cost-efficient technologies, the most important ones are extrusion and injection molding.

The emphasis laid on the areas of application and the technology of manufacturing is necessitated by the nature of the project: the possible routes of substitution, as well as the challenges the researcher has to face, primarily depend on the area of application. The greatest challenge of using microbial polyesters in the field of medical and pharmaceutical sciences is that their physical and chemical properties are more difficult to fine-tune. For example, the most important parameter of a drug carrier matrix is the time-dependent rate of the release of the drug. Kinetical parameters that determine this rate of release can be easily fine-tuned by varying the ratio of co-monomers in conventional matrices, such as polyisobutylene (PIB). Unfortunately, the ratio of co-monomers in microbial polyesters is pre-determined by the method and parameters of the fermentation.

Despite these difficulties, our research team has successfully developed a method that facilitates the production of microbial polyester-based drug carrier matrices. These matrices consist of uniformly sized particles with a very precisely variable diameter. The rate of the release of the drug is primarily determined by the diameter of the particles: the smaller the particle, the faster the release of the drug. The production of these drug carrier particles consists of two steps. The first step follows a conventional method. The second step, however, is an entirely new technology.

As a first step, particles are created by using the emulsion-suspension method. This method yields perfectly spherical particles. However, the polydispersity of this bulk of particles is unacceptably high. To overcome this difficulty, the technology of particle chromatography has been developed, which enables its user to create fractions of particles of an especially narrow distribution of diameters. Since this technology is completely new, the theoretical background required by the quantitative description of the process of separation has not been introduced yet. Therefore, a mathematical model is also proposed in the article. The model is based on the principles of rectification – exactly like the theoretical background of liquid chromatography. The article has already been successfully published.

For the reasons described in the proposal of this project, the substitution of polyolefins applied by the packaging industry was also addressed. As mentioned above, in different areas of application, different difficulties are to be faced. The most important factor that impedes the introduction of microbial polyesters to the packaging industry is that they must be processed with conventional, high-throughput techniques, e.g., extrusion and injection molding. Otherwise, the application of less productive techniques will lead to decreased output and, ultimately, increased price.

In order to maintain the competitiveness of these biopolymers on the market, extrudable and moldable materials have to be developed – strictly on a material base provided by microbial polyesters. Such a development of biopolymer-based raw materials is made possible by additives. The first and most important additive is a thermal stabilizer: as mentioned above, the conventional processing techniques share the common feature of working with the melt of the polymer. Therefore, the material must be heated above its melting temperature. At high temperatures, however, the thermo-oxidatively catalyzed degradation of the macromolecular chains occurs at a considerable rate. The dominant mechanism of the thermo-oxidative degradation of microbial polyesters is statistical chain fragmentation. As a result, the average molecular weight drops drastically, which leads to impaired mechanical performance.

In order to hinder or at least decelerate the statistical chain fragmentation, stabilizers might be used. These stabilizers can be of a synthetic or natural origin. As the proposal specifically pointed out the importance of a sustainable and circular industry, the stabilizers used in this project are of natural origins. Our laboratory has received plant extracts from a fellow research group; the materials were the product of supercritical carbon dioxide extraction. The feedstock subjected to the extraction was made of fruits; the stabilizer this project used was extracted from the peel of pomegranate.

As a result, a microbial polyester of a completely biological origin is used, stabilized by fruit extracts. The biggest challenge this methodology faces is related to the available amount of the components: the pomegranate extract was available in rather reduced quantity (a few grams). Similarly, the total amount of available microbial polyesters was in the range of a few kilograms. At this point, a technical-logistical difficulty must be highlighted, as it concerns the financial report as well. As promised in the proposal, microbial polyester was purchased (PHB-HHx) as a raw material to be used during the experiments. Unfortunately, even the smallest volume of the material sold and shipped by the manufacturer was offered at a price larger than the financial resource (material cost) for this year. Therefore, a portion of the material cost scheduled to be spent in the next year was borrowed.

As a part of the effort to keep the volumes of the materials as small as possible, the homogenization of the stabilizer in the polymer was carried out in a solution and not in bulk. This way, working with grams of the polymer and milligrams of the stabilizer became possible. From this solution, films were successfully cast, which were subsequently subjected to thermo-oxidative stress. Degradation of the samples was carried out in both heat ovens and in a laboratory-scaled press. After the degradation, the effectiveness of the stabilizer was quantitatively characterized.

First, rheological measurements were carried out. Data obtained by viscometry has proven that during degradation, the average molecular weight of the neat polymer drops drastically. However, this disadvantageous effect was mitigated considerably by the presence of the stabilizer. These findings were corroborated by the results of the mechanical tests. Compared to the reference samples that were not degraded, the neat polymer suffered a 35-50 % loss of its tensile strength. This drastic worsening was starkly contrasted by experiments carried out with stabilized samples. In the latter case, the drop in tensile strength was reduced to the 10-25 % region, which clearly highlights the effectiveness of natural stabilizers.

Besides rheological and mechanical tests, IR spectroscopy was also used to assess the efficiency of bio-stabilizers. Thermo-oxidative degradation alters the chemical structure of microbial polyesters considerably. Besides the fragmentation of the macromolecular chains already mentioned above, several side reactions also occur, which form a significant number of new functional groups on the fragments. These functional groups generally show absorbance in the infrared wavelength range. Therefore, IR spectroscopy could facilitate the monitoring and quantitative analysis of the degradation.

An important factor that limits the informativeness of one single IR spectrum is the number of side reactions and new functional groups. A number of articles that discuss the reactions that occur during thermo-oxidative degradation have already been published in the literature. They are often contradictory, but a common conclusion is made by the authors of each paper: the presence of oxygen initiates and maintains several consecutive and parallel reactions, which results in the formation of dozens of new functional groups. As a result, the entire IR spectrum of microbial polyesters is altered by the degradation; not a single absorption peak remains unaffected.

Due to the vast number of consecutive and parallel reactions taking place in the bulk of the polymer during degradation, changes in the amplitude of individual peaks cannot be traced back to individual reactions. However, an application of certain mathematical tools enables the researcher to find correlations even in the IR data of an especially complex reaction. These tools are singular value decomposition (SVD) and, based on that, principal component regression (PCR). PCR has successfully been applied during the construction of a mathematical model, which can be used to find a direct correlation between numerical data of the IR spectra and the extent of degradation.

Moreover, our measurements have proven that there is a direct (although not linear) correlation between the extent of the degradation and the yield strength of the polymer. A recognition of the existence of these correlations compelled us to combine these two: a mathematical model has been created that uses IR data to predict the yield strength of the polymer. The reliability of the model has been verified by the cross-validation method. These results provide the basis of the second article, which is currently in manuscript form.

<table>
<tr><td colspan="3">IDŐKÖZI BESZÁMOLÓ
közlemények</td><td colspan="2">NKFI-azonosító: 138430</td><td>Típus: PD</td></tr>
<tr><td colspan="3"></td><td colspan="3">Szakmai jelentés: 2022. 10. 27</td></tr>
<tr><td colspan="2">Vezető kutató:
Polyák Péter</td><td colspan="4">Kutatóhely:
Fizikai Kémia és Anyagtudományi Tanszék (Budapesti Műszaki és Gazdaságtudományi Egyetem)</td></tr>
<tr><td>Zsűri: KM2</td><td>Kezdet: 2021. 10. 01</td><td>Időszak: 2021-10-01 - 2022-09-30</td><td>Főkönyviszám: 71203</td><td colspan="2">Nyomtatás: 2023. 07. 14.</td></tr>
</table>

Sorszám	Közleményjegyzék	Dokumentum típusa	Impakt faktor	NKFI támogatás feltüntetve?	Támogató szervezetek
1.	Polyák, P., Móczó, J., Pukánszky, B.: ***Separation of monodisperse poly(3-hydroxybutyrate) particles by fractionation: Theory and practice***, Powder Technology, Volume 403, 117383, 2022	folyóiratcikk	5.640	igen	MSCA RISE No. 872152

Polyák Péter
Vezető kutató

Válasz a 138430 azonosítójú "Poliolefinek helyettesítése mikrobiális poliészterekkel" című projekt részjelentésével kapcsolatban felmerült kérdésekre

1.
PHB és PHB-HV polimerekkel kívánták a stabilitást növelő kísérleteket kivitelezni, ezzel szemben csak PHB-HHx kopolimerrel történtek kísérletek.

Válasz:
A PHB-HHx kopolimer beszerzése egy kimondottan hosszadalmas procedúra keretein belül tudott csak megvalósulni, így amíg a PHB-HHx nem állt rendelkezésre, a korábban vásárolt PHB-HV kopolimerrel zajlottak a kísérletek.

2.
Extrudálással nem készültek minták a magas alapanyagárra hivatkozva.

Válasz:
Valóban, a magas alapanyagár erősen limitálta a kísérletek kivitelezése során rendelkezésre álló polimer volumenét. Bár a PHB-HHx szignifikánsan könnyebben feldolgozható mint a PHB vagy a PHB-HV, a PHB-HHx magas ára miatt mégis érdemes maradni az eredeti tervnél és PHB-vel valamint PHB-HV-vel dolgozni.

3.
A mechanikai és TGA vizsgálatok elmaradtak.

Válasz:
Sor került mind a mechanikai, mind a TGA vizsgálatokra, azonban ezeket külön nem hangsúlyozza a részjelentés. A részjelentés arra tér ki, hogy sikerült egy olyan matematikai modellt alkotni, ami segítségével IR spektrumok alapján meghatározható a szakítószilárdság (ennek az ellenőrzése során volt szükség a mechanikai vizsgálatokra), még akkor is ha a termikus stabilitás biztosítása érdekében természetes antioxidánst tartalmaz a mátrix (a termikus stabilitás kvantitatív analízise során volt szükség a TGA mérésekre).

4.
A második évre extrudálás és fröccsöntés szerepel a munkatervben. Ha az első évben a magas alapanyagköltség miatt a nagyobb léptékű kísérletek meghiúsultak, hogyan fognak ezek a második évben megvalósulni? A magas alapanyag költség nem veszélyezteti-e a teljes projekt megvalósíthatóságát?

Válasz:
A magas alapanyagár mellett sajnos számos más tényező is hátráltatja a projektet illetve akadályozza annak megvalósíthatóságát. Mindezek miatt kiemelt figyelmet szenteltem annak hogy az első évet a vállalásaimnak megfelelően lezárjam (eredményeimet nemzetközi, impakt faktoros folyóiratban publikáltam, valamint megírtam a szakmai beszámolót), illetve hogy a második évre szánt fizetésem már ne vegyem fel. Ezt követően kezdeményeztem az NKFIH-nál a támogatotti jogviszonyom megszüntetését.