

SYNTHESIS OF SOME NOVEL POLYURETHANES AND THEIR SCOPE OF APPLICATION IN DIFFERENT FIELDS

Pranjit. Kr. Bhuyan¹, Pratap Medhi², Manisha Goswami³ and Meghna Borah⁴

¹²³⁴Department of Chemistry, Kaliabor College, Nagaon, Assam, India.

Email- prankb_tzp12@yahoo.co.in

Abstract:

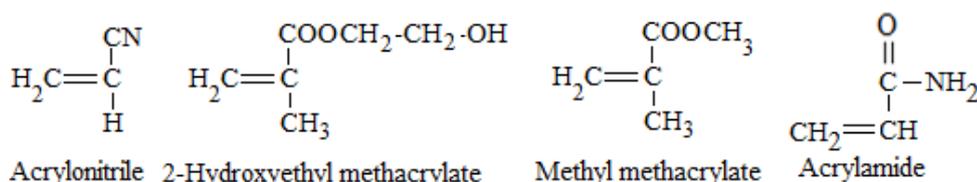
Basically polyurethanes are synthesized by reacting a diisocyanate, polyol and a chain extender diol. Once the chemical reaction of its components has taken place, the result is a polyurethane foam that is completely inert and harmless to humans. Cementitious polyurethane flooring is one of the most popular surface choices for clients working within the food and beverage sector as it offers higher strength, better heat resistance and improved chemical resistance than epoxy or MMA alternatives. Thus our choice is to synthesize some polyurethanes and its block copolymers. So, a series of polyurethane based on 4,4'-diphenylmethane diisocyanate (MDI), polypropylene glycol (PPG, M.W. 1000), 1,4-butane diol (BD) and 1,1,2,2-tetraphenylethanediol (TPED) were synthesized by the prepolymer method. The molar ratio maintained in all the synthesis was MDI:PPG:short chain diol(3:1:2). Here, MDI and PPG were reacted first thermally followed by chain extension with short-chain diols BD and TPED. Polyurethanes having such sterically hindered carbon-carbon bonds may also act as thermal macroiniferters. These thermal polyurethane macroiniferters were used to prepare polyurethane-block polyvinyl copolymers. A photoinitiator, N,N-Diethyldithiocarbamate-(1,2)-propanediol (DCPD) with a pendent N,N-Diethyldithiocarbamate group was synthesized from sodium N,N-Diethyldithiocarbamate (NaSR) and 3-chloro-1,2-propanediol(CPD). Polyurethane macrophoto iniferters having such pendent N, N-diethyl dithiocarbamate groups in its backbone were used to synthesize polyurethane-graft-poly 2-Hydroxyethyl methacrylate copolymers through photopolymerization. The photopolymerization reactions were carried out in the Heber multilamp photochemical reactor (Compact- LP-MP 88) at 254 nm. The thermal properties of both the polyurethanes and their corresponding vinyl block and graft copolymers were studied by thermogravimetric analysis (TGA).

Keywords : Block and graft copolymer, macroiniferters, polyurethane, radical polymerization, TGA, SEM.

Introduction

Polyurethanes are an important subclass of the family of thermoplastic elastomers. Due to the different polarity and chemical nature of these segments, they tend to separate into two phases usually referred to as soft and hard phases. Hard segments usually associate into hard domains because of the rigidity of the molecules and their intermolecular hydrogen bonding.

The extent of phase separation is directly related to the degree of interaction between the soft and hard segments. It has been reported that in polyester and polyether-based polyurethanes, some of the urethane N-H groups could form hydrogen bonds with the oxygen atoms of ether or ester linkages causing partial phase mixing. Polyvinyls are polymers of vinylic monomers, like styrene, methyl methacrylate (MMA), methyl acrylate, acrylic acid, acrylonitrile (AN), acrylamide etc.



The versatility of polyurethane makes it widely used in medical and pharmaceutical applications¹. There are polyurethanes that are biodegradable and harmless, and offer excellent benefits such as durability, flexibility and resistance. It also stands out for its positive biocompatibility, its resistance to bending and adaptability to different types of applications. In addition to its elastomeric properties we must add its hardness, resistance to tearing and abrasion. In fact, polyurethane is present in our lives in hundreds of forms, some directly in contact with skin or other fabrics: seats, shoes, coverings, bags, cushions, mattresses, children's toys and other surgical materials. Like all building materials, polyurethane is subject to national and European laws that guarantee the safety of building users. In the late 1970s, polyurethanes

with a wide range of permeabilities and performance as a microbial barrier were developed. Copolymerization of various monomers allows the physical and chemical properties such as water content, refractive index, hardness and oxygen permeability to be controlled. High water content lens materials are obtained by copolymerizing moderately hydrophilic HEMA with highly hydrophilic ionic monomers such as methacrylic acid (MAA) or with highly hydrophilic nonionic monomers such as *N*-vinyl pyrrolidone (NVP)². The polar lactam moiety of NVP and the ionic functionality of MAA cause these polymers to have high water contents. Thus the different types of HEMA-based contact lenses have distinct surface chemistry, surface charge and water content which influence the rate and nature of deposit formation on the contact lens surface.

Food safe polyurethane is such that it is resistant to mineral and vegetable oils, and aromatic hydrocarbons, making it a perfect choice for food grade applications. This material meets food and drug administration (FDA) requirements and national sanitation foundation (NSF) regulations for food processing applications, and is non-toxic and non-allergenic. Our food, pharmaceutical and dairy material grades have been specially developed to provide high performance food grade seals with excellent mechanical capabilities and chemical resistance. Elastomeric materials are available in several grades compliant with the requirements of the food and drug administration. In the food grade, beverage and pharmaceutical industries it is most important to choose the correct material for the particular requirements. Being one of the essential components in almost all food processing equipment and systems, the gaskets and seals have also undergone several modifications. Instead of using the gaskets and seals made from normal plastic materials, the food processing industry has started using equipment and systems with food grade gaskets and seals. This drastic move was based on the realization that most of the food contamination or sanitary issue is caused from sealing or gasket units made from poor quality materials. There is a overabundance of choices when it comes to gasket material including polytetrafluoroethylene (PTFE), polyurethane, silicone and Viton (a common name for the copolymer of hexafluoropropylene and vinylidene difluoride). Amongst these, polyurethane is chosen to make FDA accepting gaskets and seals. Many industries are turning to urethane parts and products for a variety of applications. Cast urethane offer many benefits over conventional materials such as elastomers and plastics including strength, toughness, durability, and versatility. One of the industries taking advantage of cast urethane is food processing³. The food processing sector utilizes a broad spectrum of cast urethane parts and components. Urethane products manufactured for the food processing industry include rings, gaskets, scrapers, chute liners, tabletops and custom molded FDA approved items. Food production is a demanding industry where sanitation is critical and the risk of contamination must be minimized. For these reasons, components used in food packaging and processing equipment are required to be FDA compliant. There are two main types of food processing applications that are based on the production environment: wet and dry. FDA grants approval for production equipment for either wet or dry service.

The scope of utility of polyurethanes can also be widened by its modifications. One way of modification may be its block and graft copolymerization with vinyl monomers.

A number of review articles have appeared⁴⁻⁵ to deal with the chemistry and technology of linear, branched, grafted, network polyurethanes. Linear segmented polyurethanes, which are essentially block copolymers made up of hard and soft chain segments in an alternating fashion, exhibit many of the properties of crosslinked elastomers and are of particular importance⁶

In recent years, a number of polymeric system based on reversible termination of growing radicals were reported in order to improve the radical polymerization, such as iniferters where the same species served the purpose of initiator, transfer agent and/or terminator. For controlled incorporation of vinyl blocks into polyurethane blocks, iniferter concept developed by Otsu⁷⁻⁸ can be employed.

Two types of iniferters, one is thermally and another is photochemically active, are used for block and graft copolymerization process. The C – C bond in tetraphenyl ethane moiety is sterically hindered, thermally labile and acts as a thermal iniferter. Polyurethane with this thermally labile group behaves as thermal macroiniferter⁹⁻¹³ which can be used for block copolymerization process with other vinyl monomers. Again, C – S bond is photochemically ruptured at around 254 – 366 nm and if such photo labile moieties are incorporated into polyurethane backbone then it may act as macrophotoiniferters. N, N-diethyl dithiocarbamate group is known to act as photoiniferter. When a diol with pendent N,N-diethyl dithiocarbamate group is incorporated into polyurethane backbone then it can be used to synthesise

polyurethane-graft-polyvinyl copolymers. Most of the thermal iniferters containing carbon-carbon bonds are symmetrically disubstituted tetraphenylethane derivatives.

In this paper, we describe the synthesis of polyurethane macroiniferters, both thermal (PUMI) and photochemical (PUSR) by varying the percentage of components such as TPED or DCPD and 1,4-butanediol (BD) with 4,4'-diphenylmethanediisocyanate(MDI). The Tetraphenyl ethane and its derivatives having a sterically hindered carbon- carbon single bond are known to act as thermal iniferters in free radical polymerization. The C – S bond present in dithiocarbamate group is photo chemically cleaved at around 254 – 366 nm and if such photo labile moieties are incorporated into polyurethane backbone then it may act as macrophotoiniferters (PUSR). This PUSR having pendent N,N-diethyl dithiocarbamate group can be used to synthesize polyurethane-graft-polyvinyl copolymers. The thermal stability of the resultant PU-block-polyvinyl and PU- graft-polyvinyl copolymers are characterized by TGA.

Experimental

All solvents and chemicals were purified according to the methods given in a standard text¹⁴.

2.1. Synthesis of polyurethane thermal macroiniferters based on MDI, PPG, BD and / or TPED

MDI (2.0052 g), PPG (2.6606 g), varying amount of BD and / or TPED were taken in the molar ratio 3:1:2 respectively to synthesize polyurethane macroiniferter (PUMI). MDI and PPG were reacted first at 70°C for 1 ½ h under dry nitrogen-atmosphere. The reaction mixture was cooled below to 50°C and BD and/or TPED dissolved in 20 ml methyl ethyl ketone (MEK) was added drop wise through the pressure equalising funnel. This was followed by the addition of catalyst dibutyl tin dilaureate. The reaction mixture was then again heated at 50°C for 6 hours and finally the polymer was precipitated from water. It was then dried in a vacuum oven for several days.

2.2. Synthesis of polyurethane macrophotoinitiators based on MDI, PPG, BD and /or DCPD

MDI (2.0052 g), PPG (2.6606 g), varying amount of BD and / or DCPD were taken in the molar ratio of 3:1:2 to synthesize polyurethane macrophotoinitiators (PU-SR). MDI and PPG were reacted at 70°C for 1½ h under nitrogen atmosphere. Then the temperature of the reaction mixture was lowered below to 50°C. The chain extender mixture of BD and DCPD at different compositions were dissolved in 20 ml dimethyl sulphoxide (DMSO) and slowly added from a pressure equalising funnel to the reaction mixture. This was followed by the addition of catalyst dibutyl tin dilaureate and then the reaction mixture was again heated at 90°C. At the end of six hours the reaction mixture was poured into water to precipitate the resultant polymer. It was then dried in a vacuum oven for several days.

2.3. Polyurethane- block -polyvinyl copolymers

The polyurethane with this sterically hindered carbon-carbon single bond are known to act as thermal iniferters in free radical polymerization process. They are used to synthesize a number of polyurethane-polyvinyl block copolymers. The vinyl monomers used were acrylamide (AM) and 2-hydroxyethyl methacrylate (HEMA). A mixture of polyurethane macroiniferter(PU-100%, 1.3044 g) and AM (2.0508 g) in 20 ml DMF were heated under nitrogen atmosphere at 50°C for 8 h, in constant agitation. At the end of reaction, the polymers were precipitated by pouring the mixture into methanol and then filtered. The polyurethane – block – polyacrylamide (PUMI-b-PAM) copolymers were then freed from polyacrylamide (PAM) homopolymers by washing with hot water, methanol and finally soxhlet extraction with acetone. The purified product were dried under vacuum for several days.

Further, a mixture of polyurethane macroiniferter(PU-100%, 1.3044 g) and HEMA (2.0508 g) in 20 ml DMF were heated separately under nitrogen atmosphere at 80°C for 12 hours and then the products were precipitated by pouring the mixture into large volume of water. The block copolymers were then freed from poly 2-hydroxyethyl methacrylate (PHEMA) homopolymers by soxhlet extraction with methanol. The purified product PUMI -b-PHEMA copolymer was dried under vacuum for several days.

2.4. Polyurethane- graft -polyvinyl copolymers

A mixture of PUMI (0.4157 g) and HEMA in various amount (from 0.5024) in DMSO (10 ml) was first purged with dry nitrogen. The reaction tube was then sealed and photoirradiated in photochemical reactor at 254 nm for 6 hours. The resultant polymers was isolated by precipitation in water and filtered. The graft copolymer was freed from the PHEMA homopolymers by soxhlet extraction with methanol-water system.

3. Results And Discussion

The thermal properties of polyurethane macroiniferters and their corresponding block and graft copolymers¹⁵⁻¹⁸ were characterized by thermogravimetry analysis.

Thermogravimetry analysis (TGA)

In this analysis, the mass of a sample is continuously recorded as a function of temperature. Reactions or changes that occur within the same temperature range give thermogravimetric curves that appear to consist of one continuous mass loss. A derivative mode of thermogravimetric curve termed as DTG is useful in detecting partially overlapping reactions involving the formation of weakly stable intermediates. In such cases the DTG plots give distinct peaks corresponding to each mass loss.

The thermogravimetric analysis results can be used for diagnostic purposes as no two polymers will have the same thermogram. Further, the weight loss curves may be used as a proof of the formation of copolymers. This is because the weight loss curves of random copolymers, block copolymers and graft copolymers tend to be different from each other and also from the homopolymers. The TGA- thermograms of PUMI and its block were shown in the figures 1, figures 2 and figures 3. The TGA- thermograms of PUSR and (PUSR)-g-PHEMA graft copolymer were also shown in Figure 4 and Figure 5 respectively. The difference in the nature of the thermograms indicated differences in their chemical composition which was the result of block and graft copolymerization of vinyl monomers on polyurethane backbone.

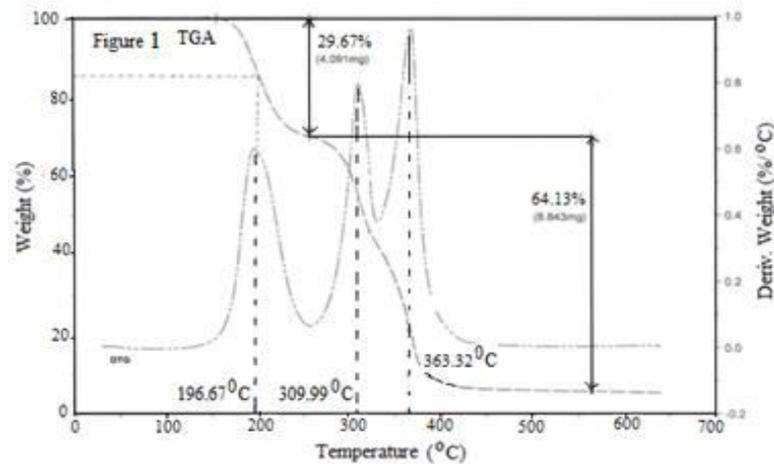


Fig. 1 TGA -Thermogram of polyurethane macroiniferter (PU-100%)

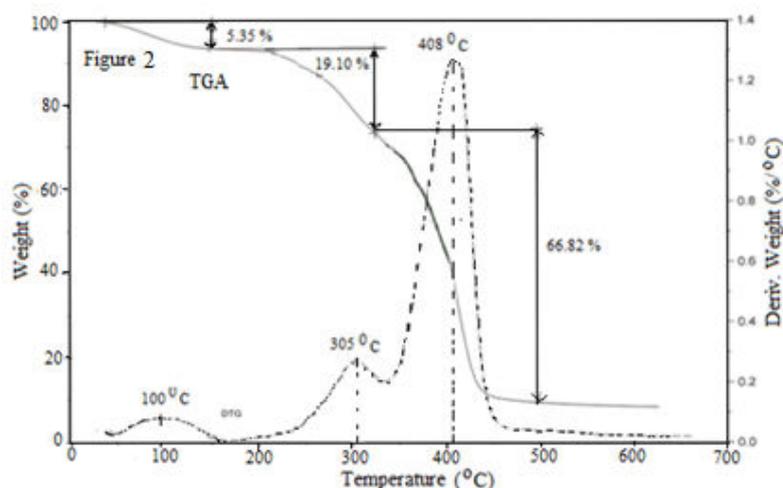


Fig. 2 TGA -Thermogram of PU₁₀₀-b-PAM copolymer

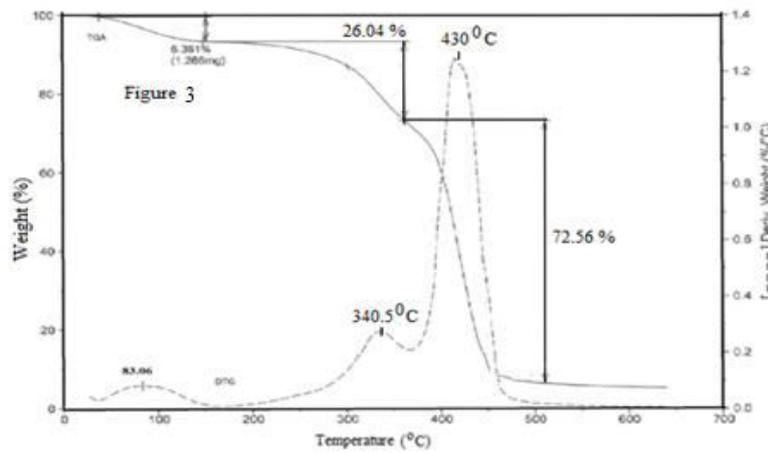


Fig. 3 TGA -Thermogram of PU₁₀₀-b-PHEMA copolymer

The TGA-thermograms of PU-b-PAM (Fig. 2) based on polyurethane macroiniferters (PU-100%) indicated two major weight loses at around 305°C and 408 °C respectively. Further, two major weight loses at around 335 to 340°C and 430°C are also observed in case of PU-b-PHEMA (Fig. 3). The weight loss patterns were distinctly different from that of the macroiniferters which showed a three-step weight loss process. The differences in the nature of thermograms again can be considered as a proof of different chemical nature of the polymers which was the result of copolymerization process. The block copolymer appeared to have a better thermal stability than that of the polyurethane macroiniferter.

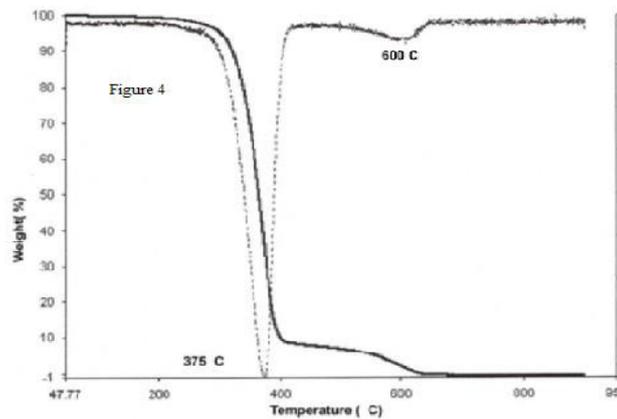


Figure 4: TGA-Thermogram of polyurethane macrophotoinitiator (PUSR).

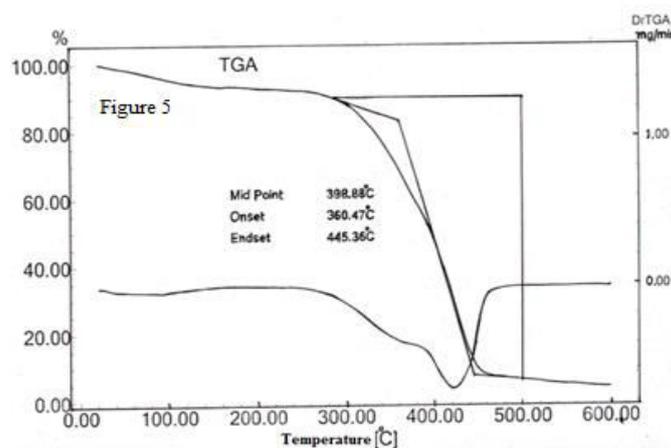


Figure 5: TGA-Thermogram of (PUSR) -g-PHEMA copolymer.

The TGA- thermograms of PUSR and (PUSR)-g-PHEMA copolymer are shown in Figure 4 and Figure 5 respectively. The difference in the nature of the thermograms indicated differences in their chemical composition which was the result of graft copolymerization of PHEMA on polyurethane backbone. The macrophotoinitiator showed the one stage degradation at 375 °C. On the other hand the graft showed degradation at 398.88 °C. Apparently the thermal stability was marginally increased as a result of graft copolymerization.

Conclusions

The study demonstrates the successful synthesis of polyurethane block and graft copolymers with the help of polyurethane macroinitiators, thermal and photo initiator. The polyurethane with the pendent N,N-diethyldithiocarbamate groups was used to synthesize (PUSR)-g-PHEMA graft copolymer. The thermal properties of polymeric materials synthesized was done by the thermogravimetric analysis. The differences in the nature of thermograms can be considered as a proof of different chemical nature of the polymers which was the result of copolymerization process. The block and graft copolymer appeared to have a better thermal stability than that of the polyurethane macroiniferters. So, It will be possible to apply this system to synthesize block and graft copolymers of choice and that polyurethane copolymers may also impart better and improved properties for their further application in different fields towards our society.

Acknowledgement

I wish to express my sincere gratitude to Dr. D. K. Kakati, Head of the Department of Chemistry, G.U. for providing the laboratory facilities and encouragement of my research work. I would like to thank the principal of kaliabor college for his good will.

I would like to thank Dr. B.K. Sharma and his scholars of Department of Chemistry, Tezpur University who helped me in recording Thermogravimetry.

References

- Gonzalez. C., D.D. Hamann. D.D. Suzanne. C. Polyacrylamide gels as elastic models for food gels. Food hydrocolloids. 1994; 8(2): 125-134.
- Megan. S. L., Martina. H. S., Anne. S., Bruce K. M. The effect of charged groups on protein interactions with poly(HEMA) hydrogels. Biomaterials, 2006; 27(4): 567-575.
- Benefits of cast urethane in food production. 2021. Accessed January 24, 2023. <https://psiurethanes.com/author/NancyE>.
- Bruins. P. F. Polyurethane Technology. Wiley(Interscience), New York, 1969.
- Buist. J. M., & Gudgeon, H. Advance in Polyurethane Technology. Wiley(Interscience), New York, 1968
- Koutsky. J. A., Hien, N. V., & Cooper, S. L. Synthesis and characterization of some polyurethane graft copolymers. J. Polym. Sci(B), 1970; 8: 353.
- Otsu. T., Yoshida. M. Role of iniferter in radical polymerization. Macromol. Chem Rapid Commun. 1982; 3: 127.
- Otsu. T., Kuriyama.A. Radical polymerization of methyl methacrylate with some 1,2-disubstituted tetraphenyl ethanes as thermal iniferters. Polym. J. 1985; 17: 97.
- Guan. J., Gao. C., Feng. L., Shen. J. Promoting the cytocompatibility of polyurethane scaffolds via surface photo-grafting polymerization of acrylamide. J. Mater. Sci. Mater. Med.2004; 12: 447.
- Yang. W., Guan. J. Enhanced irradiation self-crosslinking and co-crosslinking with nitrile rubber of poly(vinyl chloride) with pendent N,N-diethyldithiocarbamate groups. Eur. Polym. J. 1997; 33(5): 761.
- Chen. Y., Liu., P. Surface modification of polyethylene by plasma pretreatment and UV induced graft polymerization for improvement of antithrombogenicity. J. Appl. Polym. Sci. 2004; 93: 2014.
- Bhuyan. P. K., Kakati. D. K. Effect of reaction conditions on the photopolymerization of methyl methacrylate, J. Appl Polym. Sci. 2005; 98: 2320.
- Guan. J., Yang. W. Photografting of PVC containing N,N-diethyldithiocarbamate groups with vinyl monomers. J. Appl. Polym. Sci. 2000; 77: 2569.
- Perrin. D. D., Armarego. W. L. F. Purification of Laboratory Chemicals. 1stEdn.,Pergamon

- Press, New York, 1966.
15. Thermal Characterisation of Polymeric Materials. 2nd Edn., Ed. Turi. E. A., Academic Press, New York, 1997.
 16. Richardson. M. J. Comprehensive Polymer Science: The Synthesis, Characterisation, Reactions and Application of Polymers. Ed. Allen. G., Bevington. J. C., Vol. 1, Chap. 38, Pergamon Press, New York, 1989.
 17. Pielichowska K., Bieda J., Szatkowski P. Polyurethane/graphite nano-platelet composites for thermal energy storage. *Renew. Energy*. 2016; 91: 456–465.
 18. Ma R., Li W., Huang M., Liu X., Feng M. Enhancing strength and toughness of carbon fibers reinforced rigid polyurethane composites with low fiber content. *Polym. Test*. 2018; 71:156–162.