Preparation and Characterization of GF Modified Waste Rigid Polyurethane Foam

XIAOHUA GU, HONGXIANG LUO*, KE XV, WENXIANG QIU, PENG CHEN
Qiqihar University, School of materials science and engineering, 42 Wenhua Street, Qiqihar, Heilongjiang Province, China

Abstract: The preparation of polyether polyols from waste rigid polyurethane foam has been achieved by chemical degradation of ethylene glycol and diethylene glycol as the degradation agent. Then, the modified rigid polyurethane foam was prepared by polyether polyols and glass fiber. To detect the characteristic of rigid polyurethane foam, the density, water absorption, compressive strength, thermal conductivity, infrared spectrum, morphology structure had been tested. Finally, the best degradation formula was explored, and the modified rigid polyurethane foam had been prepared from the recycled polyol.

Keywords: polyurethane, degradation, glass fiber, modified, recycle

1. Introduction

Polyurethane is a kind of macromolecular organic materials with extensive application value. The properties of strength and toughness can be improved by adding inorganic filler during molecular polymerization [1]. The research of new polyurethane composites had been widely concerned. Glass fiber (GF) is an excellent performance inorganic nonmetallic material which is composed of SiO$_2$, Al$_2$O$_3$, CaO, MgO, Na$_2$O and so on [2]. In the GF preparation process, glass balls and other waste materials are melted, stretched and braided at high temperatures [3]. The annual GF consumption was relatively large, which will produce a large amount of waste difficult to treat and cause great environmental pollution. The research of GF-polyurethane nanocomposites had made a breakthrough in recent years. The impact strength of GF-polyurethane is positively correlated with the percentage of GF, but after reaching a certain peak, the impact strength of GF-polyurethane has decreased.

In recent years, the development level of the global polyurethane industry is in the stage of rapid development, which is increasing rapidly every year [4]. At present, Western Europe, North America and the Asia Pacific account for more than 85% of global production and sales, of which the Asia Pacific region has become the world's largest polyurethane market, accounting for about 45% of the global market share. The annual growth rate is 4.5%. As of 2016, China's polyurethane capacity reached 10.56 million tons, with an average annual growth rate of 5% to 7%. In the economic slowdown environment, strong growth momentum is maintained, and polyurethane materials have broad prospects for development.

Polyurethane is widely used in various fields of production and life, such as insulation sandwiches used in refrigerators, building exterior insulation boards, polyurethane rigid foams for oil pipeline transportation layers, spandex for fabrics, and polyurethane artificial leather [5-7]. Polyurethane soft foams such as car seats and mattresses, as well as polyurethane elastomers widely used in mining and machine, can substitute rubber in the industrial field.

For example, in the production of refrigerators, the rejection rate can reach 7% to 10%. In the production of other products, there are also many rejections in the production process, as well as various waste polyurethane materials such as aging products [8-10]. According to statistics, about 20% to 30% of waste polyurethane products need to be treated every year. These wastes are thermosetting polymer materials, which cannot be simply melted and reshaped, and are not easily degraded in the natural environment. It also seriously pollutes the environment while bringing problems to related companies.

*email: lhxiang2014@qq.com
How to deal with this issue economically and environmentally has become a hot topic in the industry. The recycling methods for polyurethane mainly include energy recovery methods, physical recovery methods, and chemical recovery methods [11]. Physical methods are reused after burial and simple mechanical shearing. This method causes serious environmental pollution, low economic efficiency, poor product performance and short service life [12]. Energy recovery is using polyurethane as fuel, which greatly pollutes the environment. Currently, the feasible chemical method is to treat it by alcohohysis. The alcohohysis method in the chemical recovery method has received extensive attention due to mild conditions and good performance of the reaction products [13]. One can choose the suitable alcohohysis agent and degradation conditions to obtain polyols with good quality, which can make the waste polyurethane reused [14,15]. The methods of alcohohysis and ammonolysis are widely used, while hydrolysis and pyrolysis are still in the research stage [16]. Environment-friendly materials and clean energy are the development direction of the emerging materials industry in the future. Hence, the recycling of waste polyurethane products must be carried out. Although there were many reports on the recovery of rigid polyurethane foam, the industrialization application of the chemical recycling method has not been realized, which remains in the research stage. Therefore, the recycling of waste polyurethane is imperative.

Wang J R [17] degraded polyurethane elastomer fibers and explained the degradation mechanism. Several studies in polyurethane flexible foam wastes chemical recycling are reported in the literature. Carolina Molero et al. [18] studied the glycolysis of flexible polyurethane foams with different glycols to investigate their activity and got the highest quality recovered polyol. Shameel Farhan [19] prepared carbon foam by powder molding method using waste rigid polyurethane powder. They found that the PU powder was used as a hard template without the need for subsequent template removal.

In this study, polyurethane waste (WPU) was used as material, and recycled polyether polyol was obtained by adding ethylene glycol and diethylene glycol as crosslinking agents in the degradation process. Then, foaming is carried out by mixing recycled polyether polyol with isocyanate and other additives to prepare polyurethane rigid foam (PURF). Then the GF modified PURF can be obtained by adding the GF in the process.

2. Materials and methods

2.1. Materials

Waste Polyurethane Rigid Foam(WPU); Glass Fiber(GF); Ethylene Glycol(EG), Analytical Reagent(AR), Tianjin Kemiou Chemical Reagent Co. Ltd.; Diethylene Glycol(DEG), Analytical Reagent (AR), Tianjin Kemiou Chemical Reagent Co. Ltd.; Potassium Hydroxide (KOH), Analytical Reagent (AR), Tianjin Kemiou Chemical Reagent Co. Ltd.; Polyether Polyol 4110, Chemical Pure(CP), Langfang Quanzheng Chemical Co. Ltd.; Polydimethylsiloxane, Analytical Reagent (AR), Tianjin Kemiou Chemical Reagent Co. Ltd.; Dibutyl Tin Dilaurate(DBTDL), Analytical Reagent (AR), Daian Sinobio Chemistry Co., Ltd.; Monofluorodichloroethane (HCFC-141b), Chemical Pure(CP), Shandong Binhai Chemical Co., Ltd.; Polyaryl Polymethylene Isocyanate(PAPI), Chemical Pure(CP), Wanhua Chemical Group Co.Ltd.

2.2. Experimental method

The WPU was pulverized. The degradation reactions were carried out in a four-neck reaction kettle equipped with a stirrer and refluxing condenser under N\textsubscript{2} atmosphere. The 1.0 g of KOH as the catalyst and 100 g of de-crosslinking agents composed of DEG and EG were placed in the reaction kettle, and when the KOH was completely dissolved in DEG and EG, the required quantity of WPU was added. The system was agitated with a cantilever type constant speed electric mixer at 100, 120, 140 and 160 °C in a thermostated heating jacket to obtain recycled polyol.

The variables studied were temperature (100, 120, 140 and 160°C), reaction times (1.0,2.0,3.0 and 4.0 h) and the mass ratio of DEG/EG (1/1,1/2, and 1/3). The initial time is when the PURF was completely dissolved in the de-crosslinking agents.
PURF with different contents of GF (0%, 1.0%, 1.4% and 1.8%, parts per hundred of polyol) was prepared by a one-step method, following the formula showed in Table 1. Firstly, predetermined amounts of recycled polyol, PDMS, HCFC-141b, and TEA and DBTDL were added to the polyether polyol 4110 in a polypropylene beaker and mixed under mechanical stirring at 500 rpm for 30 s to obtain a homogeneous polyol mixture. Then, a precalculated amount of PAPI and GF were added to the polyol mixture and mixed under mechanical stirring at 1000 rpm until foaming. After curing at 60°C for 20 min, the PURF were cured for at least 24 h at room temperature before performing the characterizations.

Table 1. GF Modified Waste Rigid Polyurethane Foam (GF-PU) formula

| Reactants             | Mass (g) | PPH (parts per hundred of polyol) |
|-----------------------|----------|-----------------------------------|
| Polyether Polyol 4110 | 20.00    | 66.67                             |
| Recycled Polyol       | 10.00    | 33.33                             |
| PDMS                  | 2.00     | 6.67                              |
| HCFC-141b             | 15.00    | 30.00                             |
| TEA                   | 0.07     | 0.23                              |
| DBTDL                 | 0.03     | 0.10                              |
| PAPI                  | 47.10    | 157.00                            |
| GF                    | 0.30, 0.42, 0.54 | 0, 1, 1.4 and 1.8               |

In this study, ethylene glycol and diethylene glycol, which are small-molecule alcohols, are used to degrade the waste polyurethane products. Under the effect of two alcohols, the carbamate bond is broken and substituted by a relatively short alcohol chain to forms a degradation product of the polyol. The reaction mechanism is as follows:

Reaction to breaking carbamate bond:
\[
R_1 \cdot \text{NHCOO} - R_2 + \text{HO} - R_3 \cdot \text{OH} \rightarrow R_1 \cdot \text{NHCOO} - R_3 \cdot \text{OH} + R_2 \cdot \text{OH}
\]

Reaction to producing CO₂:
\[
R_1 \cdot \text{NHCOO} - R_3 \cdot \text{OH} \xrightarrow{\Delta} R_1 \cdot \text{NH} - R_3 \cdot \text{OH} + \text{CO}_2
\]

Reaction to breaking allophanate bond:
\[
R_1 \cdot \text{NHCONH} - R_2 + \text{HO} - R_3 \cdot \text{OH} \rightarrow R_1 \cdot \text{NHCOO} - R_3 \cdot \text{OH} + R_2 \cdot \text{NH}_2
\]

The recycled polyol is then used to regenerate the polyurethane foam by the polyurethane foaming reaction. In the new foaming materials, the ether bond of diethylene glycol facilitates the formation of hydrogen bonds between the polymer molecular chains, which can enhance the polymer.

In the preparation process of polyurethane rigid foam materials, chain extension, gas generation and cross-linking branching reactions are first carried out [20, 21]. After the reaction of the polyurethane, that the diethylene glycol acts as an alcoholysis agent is contributes to forming a special-purpose polyurethane foam with some degree density, cross-linking degree and mechanical properties.

2.3 Characterization methods
The viscosity of the recovered polyol was determined by a rotary viscometer (NDJ-5S, Wuxi Xigong Tools and Measuring Co., Ltd.). This test was carried out in a glass beaker at 25°C.

An appropriate amount of recycled polyol was placed in a 100 mL Erlenmeyer flask, and the hydroxyl value was determined according to GB/TQ 128.3-2009.
The FTIR analysis was done in a spectrometer (FTS-135, American BJO-RAD Co.). Preparation of samples using potassium bromide tableting method. The FTIR spectra were acquired in the wavenumber range of 400-4000 cm\(^{-1}\).

According to QB/T 10295-2008, the thermal conductivity of the PURF was measured using the thermal conductivity tester (DRPL-III, Shanghai Jiezhuang Instrument Equipment Co., Ltd.). The thermal conductivity of three specimens per sample was measured, and the average values were calculated.

The apparent density of the PURF was tested, following GB/T 6343-1986. The apparent density of five specimens per sample was measured, and the average values were calculated.

The compression strength of the PURF was determined in a universal testing machine (HKW 50kn, Shanghai Huanke Measurement and Control Technology Co., Ltd) according to GB/T 8813-2008 with sample dimensions of 50 × 50 × 50 mm\(^3\). The compression strengths of five specimens per sample were measured, and the average values were obtained.

The cell structures of the PURF were studied. The cell structure of the PURF was observed by a polarizing microscope (A1, Carl Zeiss Jena Co). The foam sample was prepared by cutting into thin slices.

The cell structure of the PURF was studied using a scanning electron microscope (S-3400, Hitachi, Japan) at the accelerating voltage of 20 kV. The samples were prepared by a brittle fracture with liquid nitrogen and coated with gold before observation.

The water absorption rate of the PURF was determined according to GB/T 8810-88. The water absorption rate of five specimens per sample was measured and averaged.

The thermogravimetric analysis of the PURF was studied by a thermogravimetric analyzer (Q5000IR, American TA Co.). The characterization was performed from 25 to 500°C at a heating rate of 10°C/min under a nitrogen atmosphere, and the test was carried out at a gas flow rate of 50 mL/min.

3. Results and discussions

3.1. Selection of reaction time

In this study, ethylene glycol and diethylene glycol were used as alcohololytic agents in a certain proportion, and the proportion of other reactants was determined. The reaction time was set to 1.0, 2.0, 3.0 and 4.0 as experimental factors when the reaction temperature was 140°C, through the control variable method. The results of the viscosity and the hydroxyl value of the product of different degradation times under the same alcohololytic agents ratio are shown in Figure 1.

![Figure 1. Hydroxyl value of degradation products at different times](image)

The hydroxyl value of the degradation product increases as the degradation time increases. When the time is between 1.0 and 2.0h, the reaction is slow. As for 2.0 ~ 3.0h, a large amount of carbamate bond
is broken in the reactants and replaced by alcoholic hydroxyl groups, thereby the hydroxyl value is increasing faster, and the alcoholysis reaction is more intense. When the degradation time reaches 3.0 or more, the reaction tends to be gentle again, and the increasing amount in the hydroxyl value is decreases.

Considering on the comparison of the hydroxyl value of the above degradation products, the analysis shows that the requirements can be met when the degradation time is 3.0 h.

3.2. Selection of reaction temperature

In this study, ethylene glycol and diethylene glycol were used as alcohololytic agent in a certain proportion, and the proportion of other reactants was determined. The reaction time was 5h. The reaction temperature was set to 100, 120, 140, 160°C as the experimental factor. The more thorough the reaction, the viscosity of the product gradually decreased, which is shown in Table 2. When the hydroxyl value is gradually increased, the color of the obtained product is gradually deepened; when the reaction temperature reaches 140°C or above, the parameters of the degradation products are less changed. Considering the factors, the degradation temperature of the waste polyurethane is determined to be 140°C.

| temperature /°C | Viscosity/mPa·s |
|-----------------|-----------------|
| 100             | 9572.3          |
| 120             | 8112.6          |
| 140             | 6454.2          |
| 160             | 5985.9          |

3.3. Infrared spectra of degradation products

When the total amount of solution-crosslinking agent remained unchanged, the mass ratios of DEG/EG was in the range of 1/3 to 3/1, and the different degradation experiments were carried out in this condition. The optimal foaming process of the obtained oligomer polyol was studied and the obtained samples were characterized and analyzed.

Figure 2 shows the results of infrared spectra of the degradation products (DEG/EG=1/1, 1/2, and 1/3, mass ratio) and polyether 4110. Compared with the polyether 4110, the degradation products showed strong absorption bands in the range of 3500-3300 cm⁻¹, which is attributed to alcohol-based hydroxy stretching vibration peaks [22]; there is a strong absorption band near 1708 cm⁻¹, which is attributed to a benzene-type overtone peak. There is a clear and strong absorption band at 1054 cm⁻¹, which is attributed to the C-O-C absorption peak.

It can be seen that a large number of carbamates in the waste polyurethane rigid foam degradation products at 140°C are broken and substituted by the alcoholic hydroxyl group, which have been degraded into the polyols. The degree of stretching of the peak of the degradation products is similar to that of the polyether polyol, indicating that its chemical properties are similar to the polyether polyol, which proves that the polyurethane is successfully degraded.

Besides, these data demonstrate that the recycled polyol is a mixed product of a polyether polyol and an aromatic polyol. We can see that the characteristic peak of the foam (DEG/EG=1/3, mass ratio) is more obvious than others, so when the mass ratio of DEG/EG is 1/3, it may be the best formulation for degrading waste polyurethane rigid foam.
3.4. Compressive strength test

Figure 3 shows the compressive strength of the PURF with different GF additions in the different mass ratios of DEG/EG. The recycled polyol has great properties, having a rigid group such as a benzene ring and a lot of hydrogen bond [23] when the mass ratio of DEG/EG is 1/3. The PURF prepared from the recycled polyols has great properties. The reason is the grown internal strength of the PURF matrix result from the higher degree of hydrogen bonding among the urethane groups and a lot of rigid benzene rings and the better cell structure of the GF modified PURF. When the mass ratio of DEG/EG is 1/3, the GF modified PURF can withstand more strain in applications.

The GF addition had a dramatic effect on the PURF compressive strengths. The compressive strength of the PURF rose with the increasing of the GF addition in some range. In detail, the compressive strength increased sharply with a small GF addition and reached the maximum value at 1.4% GF addition. Compared with the pure PURF obtained without the GF, when the addition of GF is 1.4%, the compressive strength of the foam was increased from 0.17 MPa to 0.24 MPa, increased by 41.2%.

When the amount of GF added exceeds 1.4%, the compressive strength of PURF begins to decrease. The reason is that the cell structure of the composite with 1.8% GF was not uniform. Still, the GF modified PURF had higher compressive strength than the pure PU foam.
3.5. Apparent density test

The apparent density of PURF is shown in Figure 4. There is a large amount of gas in the PURF bubbles. The GF can act as nucleation agents and contribute to the formation of new cells. The apparent density of PURF rises with the increasing of the GF addition, when the mass ratio of DEG/EG is a constant. When the mass ratio of DEG/EG is 1/3, the apparent density of PURF with the same GF addition is the lowest and its cell is the largest. When the addition of GF is 1.4%, the apparent density of the PURF (DEG/EG=1/3, mass ratio) is 37.16 kg/cm³.

Figure 4. Apparent density of PURF with different GF addition in different DEG/EG mass ratio

3.6. Thermal conductivity test

As shown in Table 3 shows the thermal conductivity of the PURF with different GF additions in different mass ratio of DEG/EG.

| PURF formula       | Thermal conductivity (W/m·K) |
|--------------------|------------------------------|
| DEG/EG=1/1, 0% GF  | 0.0242                       |
| DEG/EG=1/2, 0% GF  | 0.0234                       |
| DEG/EG=1/3, 0% GF  | 0.0221                       |
| DEG/EG=1/3, 1.0% GF| 0.0217                       |
| DEG/EG=1/3, 1.4% GF| 0.0206                       |
| DEG/EG=1/3, 1.8% GF| 0.0213                       |

With a finer and more uniform cell structure, the GF modified PURF had a lower thermal conductivity than the pure PURF. The GF modified PURF has good thermal insulation performance and meets the requirements of national standards, and can be prepared for polyurethane products in other applications. When the mass ratio of DEG/EG is 1/3, the thermal conductivity of the PURF with 1.4% GF is 0.0206 W/m·K, having about a 6.79% decrease in comparison with the pure PURFs (0.0221 W/m·K). However, when the GF addition exceeds 1.4%, the thermal conductivity of PURF is a slight decrease. The reason is that a further increase in GF addition led to a non-uniform cell structure of the PURF.

The GF can act as a nucleation agent and serve as an area for bubble growth with the formation of new bubbles. As the amount of nucleation agents increases, the bubble size decreases, and the number of bubbles increases. Besides, GF can block the conduction of heat flow to some degree, and thus the thermal
insulation effect of polyurethane could be improved. When adding the right amount of GF, the thermal conductivity of PURF is decreases.

3.7. Polarized light microscopy analysis

Figure 5 shows the results of polarized light microscopy analysis of the obtained polyurethane foam (DEG/EG=1/3, mass ratio). It is found that the foam obtained has a larger cell structure, which is a regular polygon, and its skeleton is thick and the crosslinked structure is well, indicating that the foam prepared by the formulation has great pressure resistance. Moreover, the closed-cell that can be seen is good, and the pore film is relatively smooth and translucent, and the gas can be sealed well so that the foam has excellent heat insulation and heat preservation performance.

![Figure 5. POM images of PURF with different GF addition when the mass ratio of DEG/EG is 1/3](image)

3.8. Scanning electron microscope analysis

Figure 6 shows the SEM images of PURF with 0% and 1.4% GF addition when the mass ratio of DEG/EG is 1/3. The cell structure of the foam with 0% GF addition is even and fine, and the cell structure of the PURF with 1.4% GF addition is smaller. The GF act as a nucleation agent results in the number of bubbles becomes more than the pure PURF. Moreover, the GF also could enhance the mechanical strength of the foam cell framework. The test results are verified to have the same regularity as the results of the compressive strength of the test. Conclusively, the cell structure is vital for the mechanical properties of polyurethane foams: the superior the cell structure, the higher the strain level tolerated.

![Figure 6. SEM images of PURF with different GF addition when the mass ratio of DEG/EG is 1/3](image)

3.9. Water absorptions analysis

Figure 7 shows the water absorptions of PURF with different GF addition in different DEG/EG mass ratio. The water absorption of PURF decreased with the increase of the GF addition. The lower water
absorption presents the cell structure of the PURF is more complete and higher closed cell ratio; that is, the more gas is blocked, which result in the thermal insulation performance is better. In detail, when the mass ratio of the DEG/EG is 1/3, the water absorption of the PURF with 1.4% GF addition is 0.01792 g/cm³.

Figure 7. Water absorptions of PURF with different GF addition in different DEG/EG mass ratio

3.10. Thermogravimetric analysis

Figure 8 shows the TG curves of the different PURFs. The initial temperature of pyrolysis of the PURF increased with the reduction of the value of DEG/EG (mass ratio). The results show that the recycled polyol has better quality when the mass ratio of DEG/EG is 1/3, and it contributes to the more superior thermal stability of the PURF prepared from the recycled polyol in this condition. The initial decomposition temperature of the PURF with DEG/EG =1/3 is 231°C, having about a 10.48% increase in comparison with the PURF with DEG/EG =1/1 (210°C). The reason is when the mass ratio of DEG/EG is 1/3, there is a lot of hydrogen bond and rigid group among the molecule.

Figure 8. The TG curve of the polyurethane foams

Observing the TG curves, we found that GF could improve the thermal stability of PURF. With the temperature increasing, the weight loss rate of the sample without GF increased rapidly, but for the PURF with 1.4% GF the weight loss rate is relatively slow due to the higher chemical bond energy of the polyurethane molecule after adding GF. The PURF with 1.4% GF began to decompose at 232°C, and the...
temperature of thermogravimetric completion stage is about 500°C. Therefore, the thermal stability of the polyurethane foam can be remarkably improved after adding GF.

4. Conclusions

In this study, DEG and EG were used to treat the waste rigid polyurethane foam to obtain the recycled polyol. The PURF was prepared from the degradation products. Then, the GF was used to modify the PURF. A series of characterization analyses show that when the degradation reaction temperature is 140°C and the degradation time is 3.0h, and the mass ratio of DEG/EG is 1/3, the performance of obtained recycled polyol is the best. The presence of benzene rings in the recycled polyol plays a great role in the mechanical properties of the PURF prepared from the recycled polyol. When the GF addition is 1.4%, for the PURF prepared in DEG/EG=1/3, the compressive strength of the PURF is 0.24 MPa, having about a 41.2% increase in comparison with the pure PURF without adding GF. The thermal conductivity of the GF modified PURF is 0.0206 W/m•K, and its apparent density is 37.16 kg/cm³. The GF act as a nucleation agent led to a lot of amount of bubbles generating. Therefore, the cell structure and thermal performance of the PURF with 1.4% GF addition are finer and the water absorption of the PURF is lower.

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References
1. MARCOVICH, N.E., KURAŃSKA, M., PROCIAK, A., MALEWSKA, E. and BUJOK, S. The effect of different palm oil-based bio-polyols on foaming process and selected properties of porous polyurethanes. Polym. Int., 66(11), 2017, 1522-1529.
2. LI-PING GAO, GUANG-YAO ZHENG, YONG-HONG ZHOU, LI-HONG HU, GUO-DONG FENG. Thermal performances and fire behaviors of rosin-based rigid polyurethane foam nanocomposites[J]. Journal of Thermal Analysis and Calorimetry, 119(1), 2015, 411-424.
3. AGRAWAL A, Kaur R., WALIA R S., PU Foam Derived from Renewable Sources: Perspective on Properties Enhancement: An Overview[J]. European Polymer Journal, 95, 2017, 255-274.
4. BRZESKA J, MORAWSKA M, SIKORSKA W, et al. Degradability of cross-linked polyurethanes based on synthetic polyhydroxybutyrate and modified with polylactide[J]. Chemie Zvesti., 71, 2017, 2243-2251.
5. GIWOOK S, KIM J. H., Influence of filler surface characteristics on morphological, physical, acoustic properties of polyurethane composite foams filled with inorganic fillers[J]. Composites Science and Technology, 146, 2017, 147-154.
6. SUKRI S M., SURADI N L, ARSAD A, et al. Green composites based on recycled polyamide-6/recycled polypropylene kenaf composites: mechanical, thermal and morphological properties[J]. Journal of Polymer Engineering, 32(4-5), 2012, 291-299.
7. DAWEI JIANG, YING WANG, BIN LI, CAIYING SUN, ZHANHU GUO. Environmentally friendly alternative to polyester polyol by corn straw on preparation of rigid polyurethane composite[J]. Composites Communications, 17, 2020, 109-114.
8. GIWOOK S, KIM, S., KIM, JI, KIM J., Effect of isocyanate molecular structures in fabricating flexible polyurethane foams on sound absorption behavior. Polymer Testing, 53, 2016, 156-164.
9. PAN P, ZHU B B, KAI W., et al. Crystallization behavior and mechanical properties of bio-based green composites based on poly(L-lactide) and kenaf fiber [J]. Journal of Applied Polymer ence, 105(3), 2010, 1511-1520.
10. DATTA J, KOPCZYŃSKA, PATRYCJA. Effect of kenaf fibre modification on morphology and mechanical properties of thermoplastic polyurethane materials[J]. *Industrial Crops and Products*, 74(15), 2015, 566-576.

11. BRZESKA J, MORAWSKA M, SIKORSKA W., et al. Degradability of cross-linked polyurethanes based on synthetic polyhydroxybutyrate and modified with polylactide[J]. *Chemical Papers*, 71, 2017, 2243-2251.

12. SOBERI N S M, RAHMAN R, ZAINUDDIN F., Effect of Kenaf Fiber on Morphology and Mechanical Properties of Rigid Polyurethane Foam Composite[J]. *Materials science Forum*, (888), 2017, 188-192.

13. J. SIMON, F. BARLA, A. KELEMEN-HALLER, F. FARKAS, M. KRAXNER, Thermal stability of polyurethanes[J], *Chromatographia* 25(2), 1988, 99–106.

14. KWON, S. YANG, D. KIM, J. PARK, Characterization of Polyurethane foam prepared by using starch as polyol[J], *J. Appl. Polym. Sci.*, 103(3), 2007, 1544–1553.

15. N.V. GAMA, B. SOARES, C.S. FREIRE, R. SILVA, A. FERREIRA, A. BARROS-TIMMONS, Effect of unrefined crude glycerol composition on the properties of polyurethane foams[J], *J. Cell. Plast.* 54(3), 2017, 633–649.

16. CINELLI P., ANGUILESI I., LAZZERI A. Green synthesis of flexible polyurethane foams from liquefied lignin[J]. *European Polymer Journal*, 49(6), 2013, 1174-1184.

17. JING RONG W., DA JUN C., The Chemical Degradation Mechanism of Polyurethane Wastes[J]. *Polymer Bulletin*, (2),2004,85-90.

18. CAROLINA MOLERO, ANTONIO DE LUCAS, JUAN F. RODRÍGUEZ. Recovery of polyols from flexible polyurethane foam by “split-phase” glycolysis: Glycol influence[J]. *Polymer Degradation and Stability*, 91(2), 2006, 221-228.

19. SHAMEEL FARHAN, RUMIN WANG, HAO JIANG, KEZHI LI. Use of waste rigid polyurethane for making carbon foam with fireproofing and anti-ablation properties[J]. *Materials and Design*, 101, 2016, 332-339.

20. N. KETATA, C. SANGLAR, H. WATON, S. ALAMERCERY, F. DELOLME, G. RAFFIN, M.F. GRENIER-LOUSTALOT, Thermal degradation of polyurethane bicomponent systems in controlled atmospheres[J], *Polym. Polym. Compos.*, 13(1), 2005, 1–26.

21. DAI Z.Y., HATANO B., KADOKAWA J., TAGAYA H., Effect of diaminotoluene on the decomposition of polyurethane foam waste in superheated water[J]. *Polymer Degradation and Stability*, 76 (2), 2002, 179-184.

22. DATTA J., Synthesis and investigation of glycolysates and obtained polyurethane elastomers[J]. *Journal of Elastomers and Plastics*, 42(2), 2010, 117-127

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