Journal of Materials and Construction
ISSN 2734-9438
Website: www. jomc.vn

Research on modifying of recycling polyol from waste polyurethane foam by vegetable oil for producing insulation materials

Dam Thi My Luong[1(*)], Mai Ngoc Tam[1], Mai Trong Nguyen[1], Do Minh Thoi[1]

[1] South Vietnam Institute for Building Materials (SVIBM), Lot I-3b-5, N6 road, Saigon Hi-tech Park, Tan Phu ward, Thu Duc City, Ho Chi Minh City

KEYWORDS
Polyurethane foam waste recycling
Recycling polyol
Polyol modification
Natural oils

ABSTRACT

Polyurethane (PU) foam is formed by the condensation of 2 components Polyol and Isocyanate. PU foam waste can be recycled by glycolysis which decomposes the polymer chains into polyol. The recycled polyol can then be used as the material to make new PU foam. However, the recycled Polyol is mixed with unprofitable primary and secondary amines, and it is not suitable for use as a raw material for the production of insulating foam because of its small average molecular weight, high hydroxyl index, etc. In this study, recycled Polyol will be modified with vegetable oil for the purpose of removing the amines mentioned above, creating the product with basic properties like commercial Polyol. Research results show that the regenerated Polyol after modification has the low hydroxyl index of 423.5 mg KOH/g and the viscosity of 4400 mPa.s, which are quite similar to that of commercial Polyol and the mass average molecular weight (2440.6) much higher than regenerated polyol.

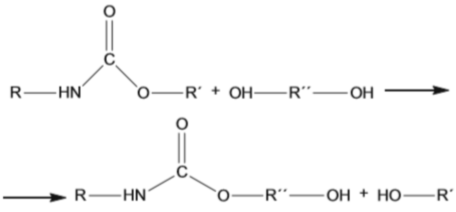
1 Introduction

1.1 Overview on recycling of PU foam by glycolysis

PU foam accounts for the largest consumption (80 % of total PU products) [1]. In particular, the rigid foam is made of closed cells, gas can exist in these cells, then the thermal conductivity coefficient is only about 0.035 W/m.K, so it is mainly used as insulation materials [2], [3], [4].

After use, PU foam can be recycled. The most researched and applied method so far is chemical recycling, the resulting regenerated polyol can replace commercial polyol to synthesize PU foam. In particular, glycolysis has the much more advantages, has been widely applied in the world and has low production cost [2], [5].

The main reaction in glycolysis between glycol agent and PU foam is as follows [6]:



The product of the process is regenerated polyol, which is a relatively complex mixture [7] including polyols, by-products (di/mono carbamate, amine), residual glycol agent [8], [9], [10]. According to many studies, regenerated polyol can be used to replace trade polyol, and the replacement content can reach 40 % [11], [12].

1.2 Overview of recycling polyol modification

According to Machado group [7], recycling polyol is limited when replacing commercial polyol: It has a very high activity, so it is difficult to control when reacting with isocyanate at high level in the reaction for the new PU foam. It contains aromatic diamine content as high as 1 %. Therefore, it is necessary to modify the regenerated polyol to reduce the activity and diamine content. According to Dai-Soo Lee group [1], aromatic amine derivatives formed during glycolysis make it difficult to control the activity of regenerated polyols.

The most commonly modifying agents are alkylene oxides, such as propylene oxide PO and ethylene oxide EO [1], [7]. PO and EO convert primary amines into secondary amines and secondary amines into tertiary amines; reduces the activity of regenerated polyols [1], [7]. In the study of Dai-Soo Lee group [1], the modified product of Jung Woo Fine Chem Co. (JWFC) has high viscosity and relatively low hydroxyl index of about 374 to 437 mg KOH/g which is very close to the commercial polyol produced by this company (450 mg KOH/g). But both PO and EO are carcinogens.

Polyol has also been studied on modifying by epoxy resin early [13], [14]. George P. Speranza group studied on the modification of polyether polyol by epoxy and alkylene oxide [13], [15], [16]. The precursor polyol (e.g. glycerine) reacts with alkylene oxide and epoxy resin step by step to lengthen the chain and increase the number of functional groups in the polyol chain. The obtained polyol has a significantly inhanced molecular weight from 2000 to 7000 then used for the production of soft PU foam [13], [15]; or has molecular weight in the range of 200 to 1000 and hydroxyl index of 125 to 1000 (usually 200 to 600) mg KOH/g to produce rigid foam [16]. According to Paul

---

[*] Corresponding author:

Received 25/04/2023, explanation 15/5/2023, Accepted 11/06/2023
Link DOI: https://doi.org/10.54772/jomc.v13i01.510

Stamberger [14], polyol modified by epoxy resin is also used to produce other kind of PU such as coating, molding material.

Thus, the modification of regenerated polyols by alkylene oxide or the modification of polyols by alkylene oxide and epoxy aims to: convert primary & secondary amines in the regenerated polyol into tertiary amines; increase the molecular weight of the product; get a suitable viscosity and hydroxyl index. To date, there has been no literature regarding the modification of regenerative polyols without alkylene oxide. In fact, there have been studies on using other materials as modifying agents, for example, using vegetable oils by Dai-Soo Lee group in the Department of Chemical Technology, Chonbuk University, Korea. Thus, the use of vegetable oils to modify regenerated polyols is a new orientation.

Tayde Saurabh [17] states that vegetable oils are fats containing triglyceride molecules. Most of these oils have a high content of unsaturated fatty acids, so they can be converted into fatty acids containing epoxy groups (three-membered epoxide ring, oxirane) by epoxidation [18]. The epoxidized vegetable oil can be used as raw material for the synthesis of many chemicals such as polyols, glycols, carbonyl compounds, and plasticizers for polymers thanks to the high oxygen content and activity of the oxirane ring [18], [19].The G.S.Sudha group [20] shows that this synthesis is done by epoxidizing vegetable oils, then transesterification reaction with alcohols such as ethanol or methanol; or acrylate reaction of epoxidized oils.

According to S. Meadows [21] and P.Saithai [22] groups, soybean oil is the most used to study on the synthesis of bio-products, especially polymer materials. The reason is large quantity, low cost and easy to convert double bonds into 3-membered epoxide groups. Enrique del Rio Nieto [23] suggests that the epoxidation of vegetable oils increases the activity and improves the properties of the materials derived from vegetable oils. The epoxidized oil can then be used indirectly or directly (as a plasticizer in the production of polyvinyl chloride PVC for example).

1.3 The purpose of the study

The aim of this study is to successfully modify the recycling polyol to obtain the product used as the substitute for commercial polyol in the manufacturing process of rigid PU foam; because the regenerated polyol contains unhelpful primary and secondary amines; the small average molecular weight, the high hydroxyl number. This study use vegetable oils to replace traditional alkylene oxides such as PO/EO as modifying agent for regenerative polyol because PO/EO is carcinogens and their use is limited.

2 Materials and research methods

2.1 Materials

In this study, the following main materials were used: commercial polyol, regenerated polyol, epoxidized soybean oil (ESO) and some other chemicals. Recycled polyol is the product made in SVIBM and has the basic properties as follows:

Table 2.1. Some basic properties of regenerated polyols.

Appearance	Density	Viscosity, mPa.s (25 °C)	Hydroxyl index, mg KOH/g
brown liquid	1.1661	740	935.2

Source: The the project team [24]

ESO oil is a commercial product made in China with the following basic properties:

Table 2.2. Some basic properties of epoxidized soybean oil.

No.	Properties	Results
1	Water content, %	≤ 0.15
2	Acid index, mg KOH/g	≤ 0.7
3	Density, ở 25 °C	0.982 đến 1.002
4	Viscosity, mPa.s (25 °C)	350 đến 450

Source: Nan Ya Plastics Corporation [25]

2.2 Research method

In the study, some standards and measurements are used to analyze and evaluate properties of raw materials and products as follows:

a, Determination of the hydroxyl number (HV) according to ASTM D 4274-A on the basis of the reaction between alcohol and anhydride in the presence of pyridine, then the amount of acetic acid formed after the reaction will be titrated with NaOH standard solution of 0.5 N.

b, Determining density according to ASTM D4669-07-A, using Czech Simax density flask (type 100 ml).

c, Determining viscosity according to ASTM D4878-15-A, using Brookfield type LVT viscometer.

d, Water content is determined according to TCVN 2309: 2009.

e, Applying GPC permeation chromatography to determine average moleculat weight of polymer.

f, Applying ^{13}C-NMR magnetic resonance spectroscopy to determine the chemical structure

g, Applying FTIR Spectra

The spectrum allows analysis of functional groups of the sample. It is possible to rely on the IR spectrum to assess the degree of conversion of the urethane group – NCOO– (according to P.Zhu [26]).

2.3 Process of modifying regenerated polyol by vegetable oil

The procedure for modifying the regenerated polyol with ESO in the reactor of 1 liter as follows:

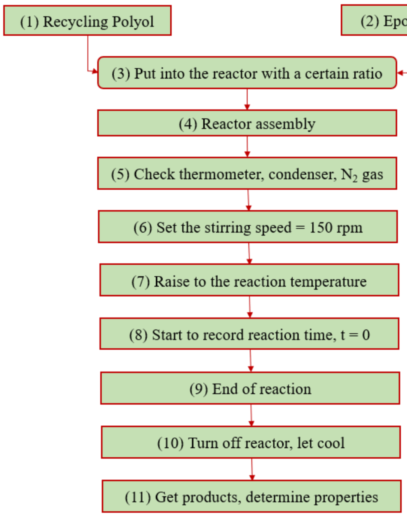


Figure 2.1. Modifying process of recycling polyol using vegetable oil.

The regenerated polyol is mixed with ESO in a certain ratio. The reaction vessel is equipped with equipments including thermometer, reflux condenser, stirrer... The reaction is carried out in N_2 atmosphere, suitable temperature for a certain period. The regenerated polyol is the product of glycolysis obtained in SVIBM under optimal conditions: glycol agent is ethylene glycol, catalyst NaOH, temperature of 198 °C and 2h [24].

3 Results and discussion

Waste PU foam can be reused for insulation materials through the recycling process. However, the use of recycling products has certain limitations, as the recycling process produces by-products, especially primary and secondary amines; the glycol agents used are monomers, so it is almost impossible for the regenerated polyol to have a large molecular weight and a low hydroxyl number. Therefore, it is not possible to directly use regenerated polyols to replace commercial polyols. The traditional method is to use common alkylene oxide such as PO and EO to modify the regenerated polyol. However, they are all carcinogens, and their use is restricted.

Therefore, to recycle waste PU foam in Vietnam successfully, it is necessary to replace the modifying agent of PO, EO. It is found that there have been long-standing researches on using epoxy resin with PO, EO to synthesize commercial polyols from the precursor polyol such as glycerine [13], [14]. In particular, there are studies on the use of vegetable oils to synthesize biopolyols [18], [19], [20], by the process as follows: epoxidize vegetable oil, then carry out the esterification reaction (transesterification) with alcohols such as ethanol or methanol; or acrylatization of epoxidized oil. Thus, it can be imagined that biopolyol synthesis from vegetable oils is quite similar to "synthesis of polyol from low-molecular precursors using epoxy and PO/EO". Epoxidized vegetable oils can be considered as epoxy derivatives. When synthesizing polyol, use epoxy with short molecular chain and combine with PO/EO to extend the molecular chain for the final polyol; When synthesizing biopolyol, "epoxy derivatives (which are epoxidized vegetable oils)" have quite large molecular chains inherited from long molecular chains of vegetable oils, so just carry out the reaction with vegetable oils. According to the groups of S. Meadows [21], P.Saithai [22], soybean oil is the most used to study on the synthesis of special biological products, especially polymer material.

The regenerated polyol produced at SVIBM is also a complex mixture in which the main components are low molecular weight polyols as common. Therefore, these regenerated polyols can be considered as monomolecular alcohols and mixed with other components. Therefore, it is possible to modify them with vegetable oil, by applying the formula of "synthesis biopolyol from vegetable oil" mentioned above, in which the alcohols are the regenerated polyols. We will use ESO to modify regenerated polyol instead of toxic PO/EO, which is not allowed to be imported into Vietnam.The study focuses on 02 objectives, (1) find out the optimal conditions for modifying reaction between the regenerated polyol and ESO; (2) appreciate the properties of the regenerated product after modification (modified product).

3.1 Investigate modifying conditions of recycling polyol by vegetable oil

Within the scope of this study, the basic factors affecting the quality of modified products will be investigated including reaction time, reaction temperature, ESO content.

Refer to the conditions for modifying the regenerated polyol by PO/EO [7]; polyol synthesis from low molecular weight precursors using epoxy and PO/EO [16]; biopolyol synthesis from vegetable oils [20]; and especially modification condition of the regenerative polyol that Dai-Soo Lee group [27] has done. Dai-Soo Lee team, which is the foreign cooperation partner of the mission, has tested the recycling of waste PU foam from Vietnam, then modified the regenerated polyol with ESO in the following conditions: 170 °C, 3h, ESO content (% mass according to regenerated polyols) is 25, 43, 67 and 100 %. Therefore, in this study, the evaluating intervals of time, temperature and ESO content compared to total input (including ESO and regenerated polyol) are: 0, 15, 30, 60, 120 and 180 minutes ; 110, 140 and 170 °C; and 25; 50 and 75 % mass, respectively.

4 Evaluation of the appropriate time for modifying reaction

When investigating the effect of reaction time on the quality of the modified products, the temperature and ESO content are fixed at 170 °C and 25 %mass. The results are evaluated through some basic properties of the obtained products as follows:

No.	Sample symbols	Time, minute	HV index, mgKOH/g	Viscosity, mPa.s	Density
1	BT-S-t1-0	0	773.1	1100	1.1562
2	BT-S-t2-15	15	740.3	1500	1.1461
3	BT-S-t3-30	30	694.3	2150	1.1342
4	BT-S-t4-60	60	678.1	3700	1.1147
5	**BT-S-t5-120**	120	672.8	4350	1.0973
6	BT-S-t6-180	180	715.6	4400	1.1189

About the hydroxyl index (HV). According to the research results of P.Zhu group [26], the regenerated polyol has quite high HV index from 847 to 875 mgKOH/g, much higher than commercial polyether polyol 455 which is 430 to 470 mg KOH/g. This is because the regenerated polyol is a mixture of polyols with a quite wide range of HV. In fact, our regenerated polyol has a rather high HV index of 933.5 mgKOH/g.

In contrast, the modified products have much lower HV values than that of the regenerated polyols. The preliminary conclusion is that ESO significantly increases the molecular weight (MW) of the modified product because the equivalent weight is inversely proportional to the HV index. The longer the reaction time, the deeper the reaction, the longer the molecular chain of the product, the lower the number of molecules with the primary hydroxyl group contributing to the hydroxyl index, the lower the HV value. However, at $t = 2h$, the product has a minimum HV value and then increases again. It can be imagined that the reaction takes place completely at 2h. As the time pass, ESO seems to be exhausted but the regenerated polyol remains, so the number of molecules with active hydroxyl increases, causing the HV value to increase.

About viscosity. The viscosity of soybean oil and regenerated polyol are low, but the modified product is much more viscous because the bonding reaction between them occurs, creates a longer molecular chain. Over time, the viscosity of the modified product increases gradually. Viscosity increases until $t = 2h$, then slightly increases. It can be seen that the modification reaction has completely occurred at 2 h. After that, the viscosity still increases but not significantly.

About density. The density of modified products is always smaller than that of regenerated polyols and larger than that of ESO. This result is consistent with the theory of the density of the mixture. As the time increases, the density of the modified product decreases, showing that the reaction gradually goes to the stage of completion without residual of regenerated polyol and ESO. When $t = 2h$, the modified product has the smallest density, then it can be considered as the optimal time of 2h. When $t > 2h$, the density of modified products suddenly changed direction, it should reflect that period of 2h is enough for the reaction. It can be explained there must be other ingredients beside modified polyol that contribute to the density of the mixture and increase the density of the mixture. It is likely that the regenerated polyol is residual so mixture's density is greater than that of the ESO.

In summary, it is found that the appropriate time is **2h**, the obtained product has the smallest HV value, the smallest density and reasonable viscosity.

5 Evaluation of reaction temperature

Evaluation of the effect of reaction temperature based on reaction time and ESO concentration of 2h and 50 % mass. The results of the product quality assessment are as follows:

No.	Sample symbols	Temperature, °C	HV index, mgKOH/g	Viscosity, mPa.s	Density
1	BT-S-NĐ 1	110	531.0	5350	1.0523
2	BT-S-NĐ 2	140	479.3	6500	1.0784
3	**BT-S-NĐ 3**	170	423.5	4400	1.0695

About the HV index. It is found that as the temperature increases, the modifying reaction occurs more completely. Therefore, it is reasonable that the HV value decreases with temperature, and is smaller than that of the regenerated polyol. The product form the reaction at 110 °C occurs delamination, it means that the reaction is not complete. Therefore, this reaction product has the highest HV. However, it is not possible to raise the modification reaction temperature more than 170 °C because the evaporation temperature of soybean oil is around this area and the optimum glycolysis temperature is 198 °C. If modifying is carried out at about 198 °C, it will affect the ability to continue to metabolize glycolysis products.

About viscosity. At 110 °C, the reaction product is separated. This shows that this temperature is not enough for the modification reaction to occur easily and completely. Thus the viscosity is almost reflective of the bottom product (more viscous) and still greater than that of regenerated polyols and ESO. It also proves that the modifying reaction has partially occurred. As the temperature increases from 140 to 170 °C, the viscosity decreases gradually. This reflects that the product viscosity of lower temperature reaction will be the greater, it means the viscosity at 140 °C is greater than that at 170 °C.

Thereby, the suitable temperature for the modification process is 170 °C, this result is similar to the study of Dai-Soo Lee group ([27]) as stated.

6 Evaluation of vegetable oil content

The results for choosing suitable ESO content for modifying reaction based on the properties of the modified products as follows:

No.	Sample symbol	ESO content, %mass	HV index, mgKOH/g	Viscosity, mPa.s	Density
1	BT-S-HL1	25	672.8	4350	1.0973
2	**BT-S-HL2**	50	423.5	4400	1.0695
3	BT-S-HL 3	75	457.7	4250	1.0310

About the HV. When the ESO content increases, it reacts enough with the regenerated polyol then obtains a modified product with a large MW, so the number of active hydroxyl-containing molecules per gram of sample will decrease, reduces the HV index of the modified product. So HV of modified product is lower than that of recycling polyol. But when the ESO content increases from 50 to 75 %mass, the HV index of the product increases again, but increases slightly. It proves that the optimum ESO content is of 50 % mass and sufficient to modify regenerated polyols.

About viscosity. ESO content increases, the modification reaction occurs stronger, obtained products have large MW and high viscosity. However, the viscosity of ESO is smaller than that of regenerated polyol, when the amount of ESO is too much, product viscosity will decrease: the viscosity of BT-S-HL 3 is lower than that of BT-S-HL 2 and even smaller than BT-S-HL 1.

About density. The amount of ESO increases, the obtained products have a decreasing density. It can be explained that when the ESO content is gradually increased, it is enough to react with the regenerated polyol, the obtained products almost contain modified product, the density is based on its contribution. Therefore, ESO content increases, the density of modified product decreases. When the ESO content is increased to 75 % mass, it may be excess, so the product contains not only modified product but also ESO. At this time, the density is based the contribution of modified product and ESO. As a result, the weight of BT-S-HL 3 is even on the downward trend compared to BT-S-HL 2.

Combination the change tendency of the HV index and the viscosity of the modified product, it is found a suitable ESO content of 50 %. This result is also quite consistent with the research of Dai-Soo Lee group ([27]).

Through evaluating the factors affect the modification process of regenerated polyol by ESO, the optimum conditions are: 2h, 170 °C and 50 % mass of ESO (compared to total input).

6.1 *Basic properties of modified regenerated polyols*

In appearance, the obtained modifying product is also a dark brown liquid but its viscosity is higher than that of the regenerated polyol. The other properties of modified products are discribed as follows:

7 Molecular weight

Determine the average molecular weight of the regenerated polyol and denatured modified products based on GPC spectroscopy as follows:

Samples	**Mn**	**Mw**	**Mp**
Recycling polyol	442.8	727.5	388.3
Modified product (BT-S-HL2)	918.4	2440.6	532.6

Mn, Mw, Mp are the number/weight/peak average molecular weight, respectively.

It is found that, thanks to the process of modification by ESO, the average molecular weight of the modified product increases significantly compared with regenerated polyol. In which, the strongest increase is mass average molecular weight with 3.4 times. This once again proves that the modifying agent ESO has improved the chain length of regenerated polyol molecules.

8 ^{13}C-NMR Magnetic Resonance Spectrum

The results of ^{13}C-NMR magnetic resonance spectrum of products are as follows:

Chemical shift, ppm	Sample	
	Recycling Polyol	Modified product (BT-S-HL2)
14.4 ppm	No	Yes
19.49 ppm	Yes	No
23.6 đến 35 ppm	No	Yes
41-50 ppm	Yes	Yes
50-80 ppm	Yes	Yes
100-150 ppm	many positions	only position of 130.66 ppm
167 ppm	Yes	No
175 ppm	No	Yes

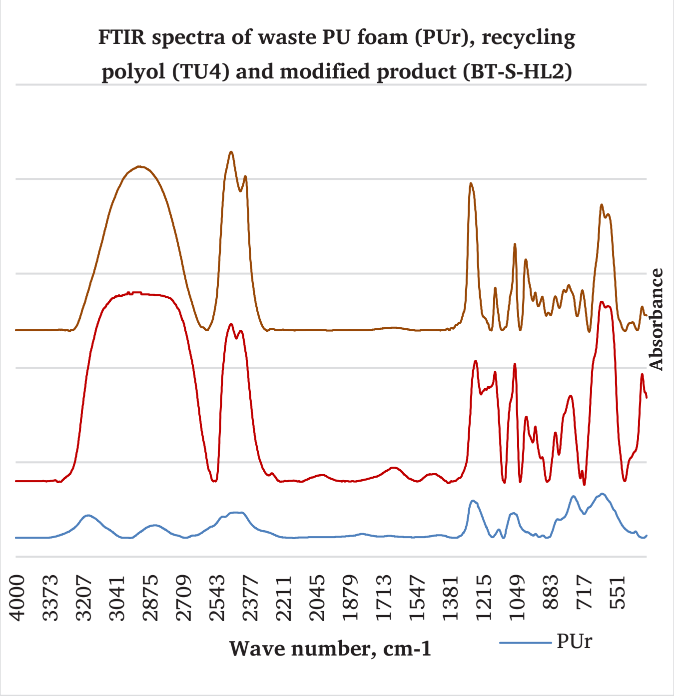
According to the research results of Se-Ra Shin group [1] : chemical shift in the range of 50 to 80 ppm involves sp3 unaromatic and saturated C, shifting from 100 to 150 ppm thanks to the contribution of sp2 unsaturated and aromatic ring C. Meanwhile, peaks of 158.6 and 162.9 ppm are observed in the carbonyl group of urethane and urea compounds.

Spectrum of the regenerated polyol appears the peak of 167 ppm, but BT-S-HL2 sample does not, it maybe the modifying process with ESO contributes to the glycolysis's completion, without the carbonyl group of the urethane and urea compound.

Peaks in the region of 100-150 ppm are characteristic in aromatic rings. There are many peak positions in spectrum of modified polyol. It can be specific to low molecular carbamate/urethane compounds/even aromatic amines. However, in spectrum of BT-S-HL2, there is only one peak of 130.66 ppm. That means modifying the regenerated polyol by vegetable oil has somewhat reduced the content of active amines.

9 FTIR spectrum

The results of structural analysis of samples through FTIR spectra are as follows:



Notably, the characteristic peak for the urethane group -NCOO- at the position of wave number of about 1724 cm^{-1} only appeares in waste PU foam samples, completely absent in regenerated polyol and modified products.

10 Water content

The free water content in the regenerated polyol and the modified product are quite similar: 6.1 and 6.8 %. It is possible that the waste PU foam has not been thoroughly dried before the recycling process. This may be the reason why the hydroxyl index of the regenerated polyol is so high compared to the commercial product. But even so, the modified product has a strongly reduced hydroxyl number and close to the commercial product. That further proves the role of the modifying process and useing ESO as a modifying agent instead of PO/EO is completely suitable.

11 Conclusion

This study is initially successful when providing a solution to use epoxidized soybean oil to replace toxic PO/EO in modifying regenerated polyol as the traditional method; overcoming the limitations of regenerated polyols. The modified product has the low hydroxyl index of 423.5 mg KOH/g and viscosity of 4400 mPa.s which are quite similar to that of commercial Polyol and a much higher weight average molecular weight (2440.6) than that of regenerated Polyol. Then this opens a new and meaningful direction in the applying waste PU foam recycling technology for insulation materials in Vietnam that has not been studied so far. Modified regenerated polyol can not only be used for the synthesis of insulation materials, but also it is an environmentally friendly material as a biopolyol.

Thank you

We sincerely thanks the financial support of the Ministry of Science and Technology for the project "Research on recycling waste Polyurethane as raw materials for manufacturing insulation materials", code NĐT.53.KR/19 .

References

[1]. Se-Ra shin, Han-Na Kim, Dai-Soo Lee, "Sustainable rigid PU foams based on recycled polyols from chemical recycling of waste PU foams (DOI: 10.1002/app.47916)," *Journal of Applied Polymer Science,* 2019.

[2]. Mir Mohammad Alavi Nikje, Amir Bagheri Garmarudi và Azani B.Idris, "PU waste reduction and recycling: from bench to pilot scales," *Designed monomers and polymers 14 (P.395-421) https://doi.org/10.1163/138577211X587618),* 2011.

[3]. Mir Mohammada Alavl Nikje (Smithers Rapra Technology Ltd), "Recycling of PU wastes," 2016.

[4]. Ron Zevenhoven (Helsinki University of Technology), "Treatment and disposal of polyurethane wastes: options for recovery and recycling," 2004.

[5]. Khalid Mahmood Zia, Hag Nawaz Bhatti, "Methods for PU and PU composites, recycling and recovery: A review," *Reactive and Fuctional Polymers 67 (P.675 - 692),* 2007.

[6]. D.Simon, A.M Borreguero, "Sustainable PU: Chemical recycling to get it (https://doi.org/10.1007/698_2014_275)," *The Handbook of Environmental Chemistry (229-260),* 2014.

[7]. Machado et al, "Process for modifying the glycolysis reaction product of polyurethane scrap (Patent number: US005300530A)," 1994.

[8]. Chao-Hsiung Wu et al, "Glycolysis of rigid polyurethane from waste refrigerators," *Polymer degradation and stability 75,* 2002.

[9]. Patrycja Jutrzenka Trzebiatowska et al, "Evaluation of the glycerolysis process and valorisation of recovered polyol in polyurethane synthesis," *Reactive and functional polymers,* 2019.

[10]. A. S. "Introduction to mechanical recycling and chemical depolymerization

(DOI: https://doi.org/10.1016/B978-0-323-51133-9.00004-8)," *Recycling of polyurethane foams,* 2018.

[11]. H. S. A. G. "Latest development for recycling of PU foam out of end-of-life mattresses into polyol for rigid PU foam application".

[12]. Michał Sołtysiński, Kazimierz Piszczek and et al, "Conversion of polyurethane technological foam waste and post-consumer polyurethane mattresses into polyols – industrial applications (DOI: dx.doi.org/10.14314/polimery.2018.3.8)".*Polimery 2018,63.*

[13]. George P. Speranza et al, "Modification of polyols with epoxy resins," *United States Patent - US 4316991,* 1982.

[14]. P. S. "Epoxxy-modified polyols and polymer-polyols useful in the preparation of improved plastics, including polyurethane foams, elastomers and the like," *United States Patent (US 4495341),* 1985.

[15]. G. P. S. e. a. "Modification of polyols with epoxy resins for use in flexible polyurethane foams," *United States Patent - US 4373034,* 1983.

[16]. G. P. S. e. a. "Polyisocyanurate from diols modified with epoxy resins (United States Patent US 4323658)," 1982.

[17]. Tayde Saurabh et al, "Epoxidation of vegetable oils: A review," *International Journal of Advanced Engineering Technology Vol. II,* 2011.

[18]. Padmasiri K.Gamage et al, "Epoxidation of some vegatable oils and their hydrolysed products with peroxyformic acid-optimised to industrial scale," *J.Natn.Sci.Foundation Sri Lanka 2009 37 (4),* 2009.

[19]. M. Y. A. "Synthesis and properties of cross-linked polymers from epoxidized rubber seed oil and triethylenetetramine," *Journal of applied polymer science,* 2015.

[20]. G. "Castor oil modified by epoxidation, transesterificationg and acrylation process: spectroscopic characteristics," *International journal of polymer analysis and characterization (http://dx.doi.org/10.1080/1023666X.2017.1334171),* 2017.

[21]. S. Meadows et al, "Studies on the synthesis and characterizaion of epoxidized soybean oil," *(https://www.researchgate.net/publication/320173456),* 2016.

[22]. P. "Effects of diferent epoxidation methods of soybean oil on the charateristics of acrylated epoxidized soybean oil-co-poly(methyl methaacrylate) copolymer," *express polymer letters vol.7, No.11 (DOI: 10.3144/expresspolymlett.2013.89),* 2013.

[23]. E. d. R. N. ""New polyurethanes from vegetable oil-based polyol" (PhD Thesis)," 2011.

[24]. P. v. V. M. N. "Chuyên đề "Nghiên cứu quá trình hóa lỏng xốp PU phế thải bằng phản ứng glycol phân tại Việt Nam"," *Đề tài "Nghiên cứu tái chế polyurethane phế thải làm nguyên liệu để chế tạo vật liệu cách nhiệt",* 2020.

[25]. N. Y. P. C. "Epoxidized soybean oil (ESO-132) - Specification sheet".

[26]. P. e. a. "Glycolysis recycling of rigid waste polyurethane foam from refrigerators," *Environmental Technology 2014-Vol 35, No. 21,* 2014.

[27]. Dai Soo Lee et al, "Báo cáo nhóm về kết quả biến tính polyol tái sinh từ xốp PU phế thải của Việt Nam, sử dụng dầu nành epoxy hóa (báo cáo nội bộ)," 2019.