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Performance characterization and pyrolysis kinetics of graphene-reinforced, green rigid polyurethane foam

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Abstract

Rigid polyurethane (PU) foam waste was chemically degraded by the two-component alcoholysis agent of diethylene glycol and ethanalamine and graphene oxide (GO), and PU/GO nanocomposites were obtained by one-step foaming. Rigid PU foam was chemically degraded by adding different proportions of two-component alcoholysis agent and GO. Research on the introduction of GO to degrade PU matrices, using different proportions of the alcoholysis agent degradation law of PU oligomer polyols for regeneration, was conducted through the viscosity and hydroxyl value of recycled polyol determination, the infrared spectrum of foam samples, x-ray photoelectron spectroscopy, density, water absorption, thermogravimetric and polarizing microscope analysis. The results showed that the compressive strength of PU/GO nanocomposites increased to 0.2754 MPa by 9.6% when the amount of graphene was 0.5% and the thermal conductivity 0.0120 W m−1·K−1, which is 4.8% reduction. The Kissinger equation was used to calculate the activation energy of the regenerated PU pyrolysis reaction. The results showed that the activation energy of the regenerated PU pyrolysis reaction was improved by adding the graphene.

1. Introduction

Polyurethane (PU) has developed rapidly since 1937 when it was developed by German scientists. Although the global PU industry is still in the development stage, different types of foam plastics, coatings [1, 2], elastomers, and plastic sealants have emerged throughout this process [3], among which PU foam accounts for the largest proportion [4]. In 2020, global PU production was 28 million tons/year, with an annual growth rate of about 4.5% [5]. The increase in PU production has also resulted in various problems, the most noticeable of which is the recycling and utilization of insoluble and infused waste PU foams [6, 7]; moreover, the environmental pollution of plastics is becoming a global problem [8, 9]. The total recycling of waste PU currently accounts for only 5 ∼ 6% [10]. The EU hopes to achieve its zero-emissions target by 2050, improving the worsening environmental crisis through green agreements [11]. The sustainable development of refractory polymer materials is the only way to achieve a closed-loop life cycle of plastics, the global carbon reduction goal, and a suitable foundation for the dual carbon goal. Therefore, the recovery and recycling of waste PU plastics are urgent [4].

PU foams can be divided into flexible, semi-rigid, and rigid forms from physical and chemical perspectives [12]. Various physical and chemical properties of the foam are endowed by polyols and isocyanates in the preparation of PU raw materials [13, 14]. In actual production [15], researchers have attempted to use alcoholysis, aminois, and biodegradation [16] to degrade waste PU foam and recover polyols due to the high cost of raw materials to partially replace the original polyols used in industry, with some progress [17].
Se-RaShin et al [18] carried out glycolysis on waste refrigerator PU foam deactivated isocyanate-derived amine adducts through propylene oxide addition polymerization, recovering two kinds of recycled polymers with different viscosities and hydroxyl values. Recycled PU foams were successfully prepared by mixing ether polyols with virgin polyols. Results showed that the PU foam prepared from the recycled polyol has better compressive strength, thermal insulation performance, and self-extinguishing performance than PU foam prepared from the original polyol.

Kopczyńska et al [19] used crude glycerol to decompose PU foam and successfully prepared glycerol lysate polyols. The resulting glycerol lysate polyol was analytically tested, and its structure and thermal properties were similar to the polyol composition used to synthesize virgin PU foam. Furthermore, they added the recovered glycerol-decomposed polyol as soft satin (SS) to the PU foam formulation, synthesizing a PU elastomer containing 16.4 wt% glycerol-decomposed polyol, which reduced the consumption of petrochemical products. It was found that the glass transition temperature increased slightly with the increase of the polyol concentration of the glycerol lysate. The experiment showed that it would not affect the thermal stability of the product when the addition of the glycerol lysate polyol reached 12 wt%.

Graphene is a new type of two-dimensional nanosheet carbon material that has attracted wide attention. Carbon atoms form a hexagonal honeycomb lattice structure with sp² hybrid orbital [20–22]; its six benzene ring structure is stable because of the graphene surface functional groups. The polymer matrix of the functional groups can form a new link and make it easier to composite applications [23] and layer between the π–π bond with excellent electrical, optical properties, good heat conduction performance, high tensile strength, electron mobility, and a low coefficient of thermal conductivity; moreover, it can adsorb and desorb various atoms and molecules [24]. Graphene is the material with the highest known strength and excellent toughness [25]. Graphene has a high aspect ratio and specific surface area, with a monolayer thickness of less than 1 nm.

Experimental results show that the incorporation of nano-graphene can significantly improve the Young’s modulus and hardness of PU materials, improving the barrier property. The composite has excellent scratch resistance and thermal insulation effect, with suitable application prospects.

In this study, waste PU rigid foam was degraded by diethylene glycol and ethanolamine. GO was introduced into the PU matrix. The waste PU was chemically degraded and modified by graphene to prepare PU/GO nanocomposites. Nanoscale graphene was chemically degraded into the degradation system of the polymer matrix to make it evenly dispersed to retain the original properties of PU and improve the barrier, mechanical properties, and strength of the foam skeleton. Nanomaterial graphene was used for the chemical degradation of PU materials, and its influence was studied. The results of this study can help explore the application of nanomaterials in the field of polymer material degradation.

2. Experimental part

2.1. Main raw materials

Waste PU rigid foam, Heilongjiang Longjiang Thermal Insulation material Co., Ltd; diethylene glycol, Tianjin Kaitong Chemical Reagent Co., Ltd, analytical purity (AR); ethanolamine, Tianjin No.1 Chemical Reagent Factory, AR; Sodium hydroxide, Alkaline Catalyst, 600mgKOH/g, Tianjin Tianli Chemical Reagent Co., Ltd, AR; Polyether Polyol (4110), Langfang Quanzhen Chemical Co., Ltd, chemical purity. Foaming agent, Shenzhen Huachang Chemical Co., Ltd, chemical purity; polyaryl polymethylene isocyanate (PAPI), Wanhua Chemical Group Co., Ltd, AR; GO, AR, Nanjing Tianshi Blue Shield Biological Co., Ltd; silicone oil stabilizer, 0.960–0.980g/cm³, Guangzhou Feirui Chemical Co., Ltd; tin solution, 90%, Beijing Zhongnuo Taian Technology Co., Ltd.

2.2. Main instruments and equipment

Analytical balance, JA3003C, Sedorius Scientific Instruments (Beijing) Co., Ltd; spherical reactor (1 l), Shandong Juancheng Hualu Electric heating instrument Co., Ltd; temperature regulating Electric heating sleeve, DRT-TW, Shanghai Baishen instrument and equipment Co., Ltd; cantilever constant Speed strong Electric Mixer, TJ-1200W, Changzhou Huaoa instrument Manufacturing Co., Ltd; Electric Mixer, JJ-IB, Shanghai Kexing instrument Co., Ltd Digital blast drying oven, WX881, Wujiang Weixin Electric heating equipment Co., Ltd.

2.3. Degradation and foaming of waste PU rigid foam

In this study, waste PU rigid foam was degraded and recycled using two-component uncrosslinking agent diethylene glycol and ethanolamine as raw materials. The waste PU rigid foam was cleaned, dried, and crushed into particles ≤2 mm. A total of 100 g diethylene glycol, ethanolamine, and 100 g of waste PU foam were proportionally weighed in a spherical reactor using an analytical balance; sodium hydroxide was added at the
same time. The temperature was raised to 180 °C, and GO was added after the foam was dissolved; the reaction continued for 3 h. The degradation products were filtered and impurities removed to obtain recovered oligomer polyols. Recycled PU thermal insulation materials were prepared by a one-step foaming method, PU/GO nanocomposites were obtained, and their properties were tested and analyzed.

2.4. Performance testing and characterization

2.4.1. Viscosity analysis
The viscosity was measured by rotational viscometer NDJ-5S. A number of oligomer polyols were placed in a designated container to test the viscosity at 25 °C.

2.4.2. Determination of hydroxyl value
An appropriate amount of oligomer polyol was placed in a 10-ml conical bottle according to the GB/T12008.3-2009 standard. The hydroxyl value was determined by ester anhydride method-pyridine.

2.4.3. Infrared spectrum test
The structure of foam samples was analyzed by FTS-135 infrared spectroscopy produced by BJO-RAD Co., Ltd. The sample was prepared by KBr pressing method, and the test wavelength range was 400–4000 cm$^{-1}$.

2.4.4. Apparent density
This test was carried out 72 h after the sample preparation according to the GB/T6343-1986 'Test of apparent density of foam and Rubber.' Five standard samples of different formulations were taken, and the average value was determined.

2.4.5. Water absorption
The sample was cut into 50 mm × 10 mm × 10 mm according to the test standard of GB/T8810-88. The water absorption was measured by distilled water. The weight of the sample was measured before and after soaking, and the water absorption was calculated.

2.4.6. Compression strength test
The size of the sheet is 50 mm × 50 mm × 50 mm, and the compression strength was tested by a WSM-20KN universal testing machine according to the standard of GB8813-2008 'Compression performance Test of rigid foam.'

2.4.7. Thermogravimetric analysis
A thermogravimetric analyzer was used to increase the test sample from 25 °C to 500 °C at a heating rate of 30 °C in a nitrogen atmosphere. A gas flow level of 50 ml min$^{-1}$ of carrier gas and alumina were selected as the reference objects, and the thermogravimetric analysis was carried out.

2.4.8. Thermal conductivity analysis
The foam sample was cut into 200 mm × 200 mm × 20 mm according to the standard of QB/T 3806-1999. The instrument was tested using a DRPL-III thermal conductivity tester made by the Shanghai Jizhun Instrument and Equipment Co., Ltd.

2.4.9. Polarizing microscope analysis
The foam sample was cut into thin slices, and the microstructure of the foam was observed using a polarizing microscope. The areas with a clear and uniform cell structure were determined, and the observation results were recorded. The microstructure was scanned and photographed.

2.4.10. X-ray photoelectron spectroscopy (XPS)
A 250XIX (American Thermo Scientific company), with monochromatic Al-Ka x-ray, and 200 W was used, working in fixed energy mode, with full and narrow scan values of 81.95 eV and 35.75 eV, with step sizes of 0.1 eV and 0.05 eV, respectively.

2.4.11. Scanning electron microscope (SEM)
The foam sample was cut into thin slices. The pore structure of the foam was studied using an SEM under an accelerated voltage of 20 kV. The samples were prepared by the brittle fracture of liquid nitrogen and sprayed with gold before observation.
3. Results and discussion

3.1. Study on the mechanism of graphene modified PU

As shown in figure 1, GO is a lattice network structure composed of benzene hexacyclic rings, and its surface has the same hydroxyl functional group as the alcoholysis agent. The regenerated polyether polyol is created by chemically degrading waste PU because the waste itself is the polymer formed by polyether polyol and PAPI. Therefore, the rigid structure of the benzene ring in the original PAPI is completely retained in the degraded regenerated polyether polyol, and the benzene ring in the degradation product is foamed in one step; moreover, it can produce a synergistic effect with the benzene six-ring rigid structure of graphene and the $\pi-\pi$ bonds existing in the layers. The materials prepared from the degradation products have better electrical and optical properties, good thermal conductivity, and high tensile strength. Tensile strength, electron mobility, low thermal conductivity, etc [26], can significantly improve the performance of recycled PU. Compared to the alcoholysis agent, GO, the hard segment brought by the introduction of the GO structure can make the small molecules of the alcoholysis agent embedded between the graphene sheets. The GO is the hard segment of the benzene ring composed of the hard segment. The structure of the nano-constrained space can be opened by the small molecules of the alcoholysis agent to expand the lamellae. The hydroxyl functional groups on the surface of GO form a good compatibility system with the hydroxyl compounds of small molecular alcohols so that small molecular alcohols are embedded between graphenes, which can initially expand the interlayer spacing of graphene [27], making small molecules. The alcohol is interspersed in the middle of the lamellar structure, beneficial to the better dispersion of inorganic graphene in the alcoholysis agent. Therefore, the GO and the alcoholysis agent have good compatibility and synergy in the degradation and foaming reactions. GO and benzene ring-containing hydroxyl compounds in waste PU degradation products form new hard segment chains in regenerated PU foam during degradation. Therefore, the evenly dispersed alcoholysis system constructed by GO and alcoholysis agent has a synergistic effect on the degradation of waste PU and regeneration of rigid PU foam products, especially the improvement of compressive strength. The white material with hard graphene segments reacts with PAPI after alcoholysis in the foaming process to form urethane, which can expand the interlayer spacing of graphene again. PAPI is relatively uniformly embedded in the graphene sheet; it is conducive to secondary dispersion and contributes to the stability of the regenerated foam in the middle of the structure. In this way, GO was successfully embedded into the regenerated PU system by chemical bonding, forming a new type of PU/GO nanocomposite.

The recycled PU foam embedding GO by chemical bonds reduces the pore size of PU foam as the PU foaming process needs to nucleate and then grow under the action of surfactant silicone oil. GO can be used as a nucleating agent to promote the foaming of recycled PU, reduce the pore diameter, and increase the amount of recycled PU foam. Moreover, it can improve the compressive strength and thermal insulation performance of

Figure 1. Degradation mechanism and preparation flow chart of go modified PU.
recycled PU foam. In addition, it has a special monatomic layered structure because the carbon atoms of GO form a two-dimensional honeycomb structure by sp2 hybridization. Therefore, it has excellent thermal and mechanical properties, and its addition can significantly improve the skeleton strength of recycled PU foam. The compressive strength of GO/waste PU composites is notably improved. The thermal conductivity, apparent density, and water absorption of GO/waste PU composites are higher than those of pure samples.

3.2. Influence of two-component de-crosslinking agent ratio on degradation products

The control variable method is used to study the experiments with different proportions of the two-component de-crosslinking agent. Under the condition that the total amount of the de-crosslinking agent is constant, the DEG:ETA ratio is set to 1:3–3:1. Different degradation experiments were carried out. The best foaming process was debugged for the oligomer polyol obtained by processing. The obtained samples were tested, analyzed, and characterized.

3.2.1. Comparative analysis of the viscosity of two-component DEG:ETA degradation products with different ratios

We obtained a series of degradation products through the experimental process and tested the viscosity of the degradation products after combining different alcoholysis agents for the alcoholysis of rigid PU foam. The results are shown in figure 2.

As seen in figure 2, compared with the commercial polyether polyol, the viscosity of the degradation product is moderate and within the general range of 4800–8000 MPa.s. The polyether viscosity is about 5000 MPa.s, and the viscosity of most components is close to that of polyether, indicating that the degradation product has suitable fluidity in actual production and has a very low dumping point [28], which is suitable for industrial production, in contrast to the ether bond contained in DEG. It is easy to form intermolecular hydrogen bonds in the process of glycolysis, resulting in the formation of diethylene glycol and solvent complexes, increasing the viscosity of the degradation products. Therefore, in the degradation process, as the content of DEG in the degraded components is high, resulting in dense cross-linking points and dense network structure, the viscosity at 3:1 is higher than that of other ratios. From the figure, DEG:ETA = 2:1 has the lowest viscosity, uniform molecular weight, and best fluidity.

3.2.2. Analysis of hydroxyl value of two-component DEG:ETA degradation products with different ratios

The hydroxyl value of the degradation product is measured so that the relationship with the molecular weight of the degradation product can be obtained. The data for analysis of the degradation material with a better foaming effect is selected from the foam product prepared by foaming the degradation material, as shown in table 1.

Table 1 indicates that the hydroxyl value of the prepared degradable material has a smaller hydroxyl value than that of polyether 4110. The overall change trend is relatively gentle, indicating that the severity of the alcoholysis reaction in each series of degradation systems is relatively different. Many carbamates undergo chemical bond cleavage and have relatively high alcoholysis efficiency [29]. The DEG:ETA ratio of 2:1 has the highest hydroxyl value, and the recovery efficiency is better than other components.
3.2.3. Infrared spectroscopy analysis of two-component DEG:ETA degradation products with different ratios

Figure 3 shows the comparison results of the infrared spectra of the degradation products obtained when the ratios of diethylene glycol, ethanolamine, and polyether 4110 are 1:1, 1:2, and 2:1, respectively. The degradation products have strong absorption bands in the range of 3500–3300 cm\(^{-1}\) compared with 4110 polyether, which are the stretching vibration peaks of alcohol hydroxyl groups \([30, 31]\). The strong absorption bands that appear near 1732–1708 cm\(^{-1}\) are benzene-type overtone peaks \([32]\). There is a strong absorption band near 1054 cm\(^{-1}\) that is a polyether-PU ether-based absorption band \([33]\). It can be concluded that the degradation products are polyether polyol and a mixture of aromatic polyols. Figure 2 shows that the characteristic peaks of DEG:ETA = 2:1 are more noticeable than others; therefore, DEG:ETA = 2:1 has the best effect as an alcoholysis agent to degrade waste PU rigid foam.

3.3. Influence of different ratios of two-component DEG:ETA on the properties of PU foam

3.3.1. Influence of different ratios of two-component DEG:ETA on foam density

The PU rigid foam prepared in this paper has the advantages of low density and high strength. The density of regenerated PU foam obtained from the foaming of degradable materials with different components of two-component DEG:ETA was measured and the results shown in figure 4. The density of the proportional foam at 3:1 is the highest, which can be attributed to the long molecular chain and high viscosity of the degradation products produced by glycolysis. On the other hand, foaming is carried out at room temperature, which significantly influences the fluidity of the degradation products; as such, the fluidity of 3:1 is poor compared with that of 2:1; foams are formed at room temperature. When part of the material is not fully reacted, it is ‘wrapped’ by the foam that has already been reacted, leading to the increase of the overall density of the foam in the later stage. Although the density of foam prepared by different proportion of two-component DEG:ETA is different, the change trend is similar, with a large gas content, large cells, and large hydroxyl value in the foam; the higher the gas content of the same volume, the smaller the density, which meets the requirements of the national...
The comprehensive conclusion is that the effect of the proportion of DEG:ETA = 2:1 in the two components is better, with larger bubbles and a lower density of 35 Kg m\(^{-3}\).

3.3.2. Influence of different ratios of two-component DEG:ETA on the water absorption of foam

The water absorption rate of foams prepared with different ratios of two-component DEG:ETA was tested, and the test results are shown in figure 5.

The water absorption of PU foam is closely related to the cell structure. The water absorption of regenerated PU foam obtained from the foaming of degradable materials with different components of two-component DEG:ETA was measured and the results shown in figure 5. The water absorption of the rigid PU foam prepared by the two-component formula is in line with the national standard, with a suitable foam performance; the lower the water absorption rate, the more complete the cell structure of the foam, and the higher the closed cell rate of the foam, which is similar to the infinite heat shield effect, effectively restraining the reflection, scattering, and absorption of thermal radiation; this locks up more gas. The thermal insulation performance and thermal insulation performance of the prepared PU foam are better. The water absorption of the 3:1 component in figure 5 is the highest, indicating that the foam cell of this component is uneven and the closed cell property is poor; this is because the degradation material obtained by glycolysis has high viscosity. The high viscosity in the foaming process hinders the mixing of black material and white material, making the mixing uneven, resulting in a large water absorption rate.
in an uneven bubble cell and even rupture; therefore, its water absorption is higher, while the viscosity of the degradation material obtained by glycolysis of other components is lower than 3:1. Therefore, as the fluidity is better, the foaming mixture is more uniform, the cells are relatively intact, and the water absorption is 0.016 g cm\(^{-3}\) when DEG:ETA = 2:1. At the same time, the figure also echoes figure 4. By synthesizing the density, water absorption, and pressure resistance between the two-component formula foams, the proportion of DEG:ETA = 2:1 shows better comprehensive properties.

3.3.3. Effect of different ratios of two-component DEG:ETA on the compressive strength of foam

The prepared foam is cut into 50 mm \(\times\) 50 mm \(\times\) 50 mm samples according to the test standard, and the compressive strength is measured by the instrument to obtain the strength of different foams. As an important index to evaluate the properties of PU rigid foam, compressive strength plays a key role in the testing of PU rigid foam. The compressive strength of the recycled PU foam obtained after foaming the degradable materials of two-component DEG:ETA with different components was measured and the results shown in figure 6. According to the analysis of the test results, with the change of the proportion of alcohol, the compressive strength of the foam constantly changes, and the strength of the two-component DEG:ETA = 3:1 foam is the lowest. From the viscosity of the degradable material, the water absorption of the foam and the SEM test it can be seen that the foam with the 3:1 ratio has an uneven cell distribution and serious ruptures, indicating that its compressive strength is the lowest. When the two-component DEG:ETA = 2:1 foam strength is 0.25 MPa, the cell is complete, it is regular hexagonal in shape, and has strong skeleton and suitable cross-linking density, indicating its excellent compressive strength. The prepared foam can fully meet the national standards and has adequate compressive properties.

3.3.4. Thermogravimetric analysis of foams with different ratios of two-component DEG:ETA

The prepared foams were eliminated and selected, respectively, based on the density, water absorption, compression resistance, and other conditions. Two groups of foams with DEG:ETA ratios of 2:1 and 1:2 were determined to perform thermogravimetric analysis as shown in figure 7.

Figure 7 shows that the weight loss of two-component DEG:ETA = 1:2 and DEG:ETA = 2:1 foam begins at about 225 °C, and the thermal weight loss of two-component DEG:ETA = 1:2 foam is noticeable at 324 °C. The two-component DEG:ETA = 2:1 foam is noticeable at 340 °C, indicating that the chemical bond energy of the PU molecules in the DEG:ETA = 1:2 system is relatively low, and the chemical bond is easy to break [34] and that the thermodynamic stability is low. However, the intermolecular chemical bond energy of PU in the two-component DEG:ETA = 2:1 system is relatively high, the crosslinking density is acceptable, the hydroxyl value is high, the number of hydrogen bonds is large, and it is not easily decomposed. The chemical bond is easy to break, indicating good thermal stability [35]. Therefore, the foam prepared by two-component DEG:ETA = 2:1 degradation products in the two systems is the highest in the starting temperature. The peak temperature and end temperature of thermal weight loss indicate that its thermal stability is the best of the two groups. The thermal weight loss temperature of foam prepared by two-component DEG:ETA = 2:1 degradation products is
340 °C, 16 °C higher than that of two-component DEG:ETA = 1:2 degradation products. Therefore, the foam prepared by two-component DEG:ETA = 2:1 degradation products has the best thermal stability up to 340 °C.

3.3.5. Thermal conductivity analysis of two-component DEG:ETA foam with different ratios
To further analyze the performance of the prepared two-component DEG:ETA foams with different ratios, the thermal conductivity of the two-component and three-component series of foams was measured in this experiment, as shown in the table.

Table 2 shows that the difference between the thermal conductivity of the foams prepared by the two series is relatively small. The standard of the thermal conductivity of the known PU foam is lower than 0.03 W/mK. The thermal conductivity of the prepared foams is all lower than 0.03 W·m⁻¹·K⁻¹. The DEG:ETA = 2:1 series has the lowest thermal conductivity, 0.0126 W·m⁻¹·K⁻¹, and suitable thermal insulation.

3.3.6. Effects of different ratios of two-component DEG:ETA on the foam cell structure
It was roughly determined that the rigid foam with better performance in the whole system is selected through the visual observation and pressing of the foam, and the foam is cut into thin samples. The lens screenshot after the sample is magnified 20 times. An area with a clear field of view and well-ordered cells for observation was selected, as shown in figures 8 and 9.

As shown in the figure, the foam has a larger cell structure, regular hexagonal structure, a strong skeleton, good cross-linking structure, and suitable geometric structure [36] when the ratio of DEG:ETA is 2:1. This indicates that the foam prepared by this formula has high compressive properties. However, the cell structure of DEG:ETA = 3:1 is irregular, the skeleton is slender, the cross-linking is unsuitable, and the strength is low. The cross-linking degree of DEG:ETA = 2:1 series foam can provide better compressive strength for the foam, saving raw materials while having the same strength. Moreover, the pore film is relatively smooth and bright and can sufficiently seal the gas so that the foam has an excellent thermal insulation and thermal insulation performance.
3.4. Analysis and characterization of GO/PU composites

3.4.1. Preparation process of GO/PU composites
Based on the previous results, the degradable material of DEG:ETA = 2:1 series is selected, and GO is added to modify the regenerated PU foam. The specific preparation process is shown in figure 10.

3.4.2. FT-IR analysis of GO/PU composites
Figure 11 shows the infrared spectra of pure PU and PU/graphene. The 3500–3250 cm$^{-1}$ is the stretching vibration absorption peak of $\text{-OH}$. The 2280–2260 cm$^{-1}$ is the asymmetric stretching vibration peak of $\text{-NCO}$, which is the characteristic isocyanate group of PU. The vibration peak intensity is weakened after adding graphene, indicating that the functional group on the graphene structure reacts with the isocyanate group to form a new group. The 1540–1530 cm$^{-1}$ value is the characteristic peak of $\text{–CO–NH–}$, indicating that $\text{–NCO}$ and $\text{–OH}$ react. The carbamate group is generated, the content of $\text{–NCO}$ decreases, and the intensity of the characteristic peak weakens. The 1750 cm$^{-1}$ is the stretching vibration peak of C=O. The 1320–1220 cm$^{-1}$ and 11151080 cm$^{-1}$ are the asymmetry of $\text{C–O–C}$ stretching vibration absorption peaks [37]. The various absorption peaks of the two curves in the figure did not change significantly. Although no new functional groups were generated, the $\text{–NCO}$ characteristic peak was weakened, indicating that the addition of graphene would not affect the overall PU structure.

3.4.3. XPS analysis of GO/PU composites
XPS can be used to determine the composition of elements in materials and the chemical and electronic states of the elements contained in them. XPS characterization analysis was performed on PU and PU/GO. Figure 12 (a) and (b) are the C1s photoelectron spectra in pure PU and PU/GO, respectively. Figure 12 (c) is the XPS full spectrum of PU and PU/GO, which shows that there are also characteristic peaks of N1s in addition to C1s and O1s. Figure 12 (a) shows that there are characteristic peaks of CC (284.8eV), CO (286.4eV), C=O (287.1eV),
and OC=O (288.9eV, originating from the carboxyl group) in pure PU. Figure 12(b) is the same as figure 12(a). There are two new absorption peaks, CN (285.3eV) and O=CN (287.2eV) in addition to the original characteristic peaks. Figure 12(c) shows that the content of C, N, and O elements increases after adding GO [38]. It can be preliminarily confirmed that there is an amide group (–CO–NH–) that corresponds to the infrared analysis results. The above results show that GO has been grafted into the PU system, and PU/GO nanocomposites have been successfully prepared.
3.4.4. Compression strength Test of GO/PU composites

Table 3 shows the data of compressive strength, foam density, thermal conductivity, and water absorption of DEG:ETA = 2:1 with different GO content. The additional amounts of GO are 0.25%, 0.5%, and 1.0%, and its strength is greater than that of 0.2512 MPa (0% GO). When the addition of GO is 0.5%, the maximum strength is 0.2754 MPa, increased by 9.6%, and the thermal conductivity is 0.0120, which is reduced by 4.8%. The apparent density and water absorption are the same as those without GO and remain unchanged. Graphene is embedded in the crosslinked network structure formed by polyether and isocyanate during the formation of PU, which enhances its skeleton structure and is consistent with the results of theoretical mechanism analysis.

3.4.5. SEM analysis of GO/PU composites

Figure 13 shows an SEM test chart of the effect of graphene nanomaterials on the morphology and distribution of polymer modification. Figure 13(a) shows the test chart of the pure sample. The surface of pure PU is smooth, without any impurities, and lessened fracture. Figure 13(b) is the GO/PU composite foam diagram. The prepared PU foam has a white texture, no scum on the surface, and a fine arrangement of foam cells.
Figure 13(C) shows that the number of micropores increased, and no obvious particles or deposits were observed. It can be seen that graphene has been well dispersed in the PU matrix. However, there is also a partial agglomeration phenomenon, which only increases the pore size and does not lead to the rupture of the bubble because graphene plays a supporting role on the pore wall. The interface is blurred, and there is noticeable folding at the edge, indicating that the bonding strength is better, and the closed porosity is higher.

Figures 13(a)–(c) indicates that the skeleton of the regenerated PU foam formed after the addition of graphene is stronger than before addition. This is because graphene is embedded in the cross-linked network structure formed by polyether and isocyanate during the formation of PU, consistent with the mechanical analysis results.

3.4.6. Thermogravimetric analysis of GO/PU composites

Comprehensive density, water absorption, pressure resistance, and other conditions for the preparation of foam elimination selection determined that the addition of 0.5% GO when the proportions of DEG:ETA are 2:1 and 1:2 results in two foam groups with better performance confirmed by thermogravimetric analysis, as shown in figure 14.

The figure indicates that the thermal weight loss of two kinds of foam can be divided into three stages. The first stage is 100 °C–200 °C. The evaporation of free water and bound water in the foam leads to the weight loss of the foam. The second stage is at 200 °C–390 °C. This stage is the fracture of isocyanic acid and hard segment in the PU segment. The third stage is 390 °C–580 °C. This stage is the fracture of polyether SS in the PU tip. The mass loss temperature of the foam prepared by the two ratios is about 230 °C. The decomposition stops at about 580 °C. The temperature of the fastest weight loss of DEG:ETA = 1:2 is about 328 °C, while that of DEG:ETA = 2:1 is about 347 °C. The weight loss rate of DEG:ETA = 1:2 is notably faster than that of DEG:ETA = 2:1 in the local magnification area, indicating that the chemical bond energy of foam prepared by DEG:ETA = 2:1 is higher than that of DEG:ETA = 1:2. Therefore, it can be concluded that the foam prepared by DEG:ETA = 2:1 is more stable.

3.4.7. Pyrolysis kinetic analysis of GO/PU composites

The Kissinger method will be used to analyze three different heating rates (5 K, 10 K, and 20 K) of the recycled PU foam with RPU/GO (DEG:ETA = 2:1) component and RPU pure sample. Then, the activation energy Ea of the
The pyrolysis reaction will be calculated. The pyrolysis kinetic parameters obtained from TG and DTG curves are shown in Table 4.

Figures 15(A) and (B) show that the maximum thermal loss focus of the PU foam continues to shift to the high-temperature zone with the increase of the heating rate; the higher the heating rate, the shorter the reaction time and the lower the reaction degree of the PU foam, as it affects the internal heat transfer of the regenerated PU foam. This shows that the DTG curve shifts to the high-temperature zone.

Firstly, the general form of the Kissinger equation to obtain the activation energy of pyrolysis from the Kissinger equation is as follows:

\[
\frac{d\ln(\frac{\beta}{T_p^2})}{dT_p} = -\frac{E}{R}
\]

(1)

The following form can be obtained by applying the Kissinger equation to the pyrolysis kinetic equation.

\[
\ln(\frac{\beta}{T_p^2}) = \ln RA - \frac{E}{RT_p}
\]

(2)

In Formulas (1) and (2):
- \(\beta\)–Heating rate
- \(T_p\)–Peak temperature in DTG curve
- \(E\)–Apparent activation energy
- \(A\)–Pre-exponential factor

In Formula 2, \(1/T_p\) is plotted with \(\ln(\beta/T_2p)\), and a straight line is obtained by linear fitting, as shown in figures 14 (a) and (b). The correlation coefficient of the fitting line and the pyrolysis activation energy
Ea = 102.30 KJ mol⁻¹ obtained by calculating the slope are finally obtained. The activation energy of the pyrolysis reaction of RPU/GO composites is Ea = 187.29 KJ mol⁻¹. The activation energy of the pyrolysis reaction of RPU/GO composites increases with the addition of nano-GO, indicating that the thermal stability of RPU/GO composites has been improved [40]. In later use, the foam can be considered stable.

4. Conclusion

In this study, waste PU was successfully degraded by DEG and ETA. A regenerated polyether polyol similar in structure and performance to polyether polyl 4110 was obtained; it can be used as the raw material for PU synthesis. The rigid PU foam with low density, high thermal insulation, and compression resistance was prepared when DEG:ETA = 2:1. The density was 35 kg m⁻³, the water absorption rate 0.016 g cm⁻³, the compressive strength 0.2512 Mpa, and the thermal conductivity 0.0216 W m⁻¹ K⁻¹. GO was successfully grafted into the PU system, and the waste PU foam degradation system was chemically modified by GO. The thermal stability of the PU/GO composite was 6.45% higher than that of the pure sample. The addition of graphene lengthens the heat transfer path and reduces heat loss; the optimal addition of graphene is 0.5%, and the compressive strength of the foam increases by 9.6%. The thermal conductivity is reduced by 4.8%. Its density and water absorption are the same as those without GO. The activation energy of the pyrolysis reaction of recycled PU calculated by the Kissinger equation was E = 187.29 KJ mol⁻¹ at three different heating rates of RPU/GO composites. This indicates that the addition of graphene increased the activation energy of PU, and the activation energy increased ΔE = 84.99 KJ mol⁻¹. However, the activation energy of GO/PU recycled PU material is still within the range of the pyrolysis activation energy of PU rigid foam. The analysis and research of the nanomaterial graphene for the chemical degradation of PU materials have important guiding significance for future research.
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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References

[1] Ou et al. 2018 Preparation of novel marine antifouling polyurethane coating materials Polym. Bull. 75 5143–62
[2] Rahman et al. 2019 Water-erosible santhan-acrylate-polyurethane antifouling coating Polymers 11 1700
[3] Xu et al. 2021 Lignin-based polyurethane: recent advances and future perspectives Macromol. Rapid Commun. 42 2000492
[4] Deng et al. 2021 Reviewing the thermo-chemical recycling of waste polyurethane foam J. Environ. Manage. 278 115127
[5] Zhao L and Semety V 2021 Recycling polyurethanes through transcarbamoylation ACS Omega 6 4175–83
[6] Van Bergen et al. 2020 Recycling of flexible polyurethane foam by split-phase alcoholysis: identification of additives and alcoholizing agents to reach higher efficiencies ChemSusChem 13 3835–43
[7] Heiran et al. 2021 Glycolysis: an efficient route for recycling of end of life polyurethane foams J. Polym. Res. 28 22
[8] Cole et al. 2011 Microplastics as contaminants in the marine environment: a review Mar. Pollut. Bull. 62 2588–97
[9] Kemenas and Piotrowska 2020 Polyurethane recycling and disposal: methods and prospects Polymers 12 1752
[10] Akindoye et al. 2016 Polyurethane types, synthesis and applications - a review RSC Adv. 6 114453–82
[11] Bartolo et al. 2021 A Review of Bioplastics and Their Adoption in the Circular Economy 13 1229
[12] Gama et al. 2020 Recycling of polyurethane scraps via acidolysis Chem. Eng. J. 395 125102
[13] Zia et al. 2007 Methods for polyurethane and polyurethane composites, recycling and recovery: a review React. Funct. Polym. 67 673–92
[14] Nikje et al. 2020 Preparation and application of glycolysed polyurethane integral skin foams recycle from automotive wastes Polym. Bull. 36 255–65
[15] Simon et al. 2018 Recycling of polyurethanes from laboratory to industry, a journey towards the sustainability Waste Manage. (Oxford) 76 147–71
[16] Magnin et al. 2020 Evaluation of biological degradation of polyurethanes Biotechnol. Adv. 39 107457
[17] Godinho et al. 2021 Recycling of different types of polyurethane foam wastes via acidolysis to produce polyurethane coatings Sustain. Mater. Technol. 29 e00330
[18] Shin et al. 2019 Sustainable rigid polyurethane foams based on recycled polyls from chemical recycling of waste polyurethane foams J. Appl. Polym. Sci. 136 17916
[19] Kopczynska et al. 2016 Synthesis and characterisation of polyurethane elastomers with semi-products obtained from polyurethane recycling Eur. Polym. J. 85 26–37
[20] Zhu et al. 2021 Current advances of polyurethane/graphene composites and its prospects in synthetic leather: a review Eur. Polym. J. 161 110837
[21] Lui et al. 2009 Ultraflat graphene Nature 462 339–41
[22] Grigorenko et al. 2012 Graphene plasmonics Nat. Photonics 6 749–58
[23] Han et al. 2014 Preparation of polyurethane nanocomposites via covalent incorporation of functionalized graphene and its shape memory effect Composites Part A 58 65–72
[24] Jing et al. 2018 Preparation and characterization of isocyanate functionalized graphene oxide/thermoplastic polyurethane elastomer composites J. Macromol. Sci.-Phys. B 58 425–41
[25] Kausar et al. 2019 Shape memory polyurethane/graphene nanocomposites: Structures, properties, and applications Journal of Plastic Film and Sheeting 36 151–66
[26] Liu et al. 2019 Novel graphene oxide/per/1.4-polyisoprene (GO/TP) shape memory polymer nanocomposite and its multifunctional properties Nanotechnology 30 255706
[27] Xi et al. 2016 Graphene oxide membranes with strong stability in aqueous solutions and controllable lamellar spacing ACS Appl. Mater. Interfaces 8 13557–66
[28] Gu et al. 2021 Effect of different catalysts on recovery and reuse of waste polyurethane rigid foam Mater. Res. Express 8 035105
[29] Wang et al. 2011 Chemical degradation of thermoplastic polyurethane for recycling polyether polyol Fibers & Polymers 12 657–63
[30] Nikhe et al. 2007 Chemical recycling and liquefaction of rigid polyurethane foam wastes through microwave assisted glycolysis process J. Macromol. Sci.-Part A 44 613–7
[31] Xiao et al. 2019 Effect of small molecule alcohol on recovery and recycling of waste PU hard foam China Polym. Sci. 33 84–8
[32] Borowicz 2021 Effect of New Eco-Polyls Based on PLA Waste on the Basic Properties of Rigid Polyurethane and Polyurethane/Polysioacurate Foams Int. J. Mol. Sci. 22 8981
[33] Reiner 2020 TG/DTA-FTIR as a method for analysis of tall oil based rigid polyurethane foam decomposition gaseous products in a low oxygen environment Polym. Degrad. Stab. 180 109313
[35] Günther M, Levchik S V and Schartel B 2020 Bubbles and collapses: Fire phenomena of flame-retarded flexible polyurethane foams Polym. Adv. Technol. 31 2185–98
[36] Nelson M C 2003 The Relationship of Cell Morphology, Density, and Mechanical Properties in a Rigid Polyurethane Foam (University of Nevada: Las Vegas)
[37] Jiao L et al 2013 Thermal degradation characteristics of rigid polyurethane foam and the volatile products analysis with TG-FTIR-MS Polymer Degradation & Stability 98 2687–96
[38] Chen Y et al 2019 Structure and Flame-Retardant Actions of Rigid Polyurethane Foams with Expandable Graphite Polymers 11 686
[39] Mikulić H et al 2019 Thermogravimetric analysis investigation of polyurethane plastic thermal properties under different atmospheric conditions Journal of Sustainable Development of Energy, Water and Environment Systems 7 355–67
[40] Chen X, Li J and Gao M 2019 Thermal degradation and flame retardant mechanism of the rigid polyurethane foam including functionalized graphene oxide Polymers 11 78