Performance of supercritical methanol in polyurethane degradation

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Abstract. Polyurethane is a group of block copolymer which is composed of diisocyanate, chain extender, and polyol, including polyurethane foam, polyurethane elastomer, waterborne polyurethane, etc. This research focused on thermoplastic polyurethane elastomer (TPU) which is formed with 4,4'-diphenylmethane diisocyanate(MDI), poly(1,4-butanediol-hexanedioic acid) diolpolyester(PBA) and extended with 1,4-butanediol(BDO). The degradation of TPU was carried out with the help of methanol as the supercritical solvent. The SEM of the reaction residues revealed the process of the depolymerisation. The products were measured by GC-MS and found out to be PBA, BDO and 4,4'-methylene diphenyl carbamate (MDC) which is the methyle of MDI. GC-FID, HPLC-UV and GPC were used to further analysis. The experimental results showed that supercritical methanol performed outstandingly in TPU recycling, it needed lower temperature and shorter time than regular methods. At 230 °C/70min, over 90% raw materials of TPU could be recovered .

1 Introduction

Polyurethane (PU) is composed of diisocyanate, polyether polyol or polyester polyol, and chain extender [1]. The property and utilization of PU could be manipulated by varying the raw materials. Consequently, it is one of the most promising polymers. Its products include rubber, fibre, resin, tackiness agent, coating material and functional polymer.

Recent chemical recycling methods of PU contain pyrolysis, hydrolysis, glycolysis [2-4], aminolysis, and hydrogenation et al. Among the above methods, glycolysis has more advantages in industrial applications because of the broad adaptability and mild reaction conditions. However, the glycolysis only recovers the polyol from PU, and needs 2~5h to complete the degradation reaction. The products are complicated and difficult to separate.

Supercritical methanol($T_c=239\text{ }^{\circ}\text{C}$, $P_c=8.1\text{MPa}$)has moderate critical condition, weak hydrogen-bond interaction, and high dielectric constant. It performs excellently in polymer dissolving and extracting [5, 6]. It's an important replacement of supercritical water in polymer recycling. Especially in the depolymerization of the condensation polymer (such as PET [7, 8], PC [9], PBT [10, 11]), supercritical methanol not only plays the role of the solvent, but also participates in the scission of the polymer chain as the reactor. Besides excellent transmission characteristic and dissolution characteristic, it also has splendid reaction characteristic.

In this work, thermolysis was compared with supercritical methanolysis, in order to investigate the feasibility and effectivity of the later method, study of

TPU degradation behavior in sub-/supercritical methanol was carried out. By analysis and calculation, we found the maximum yield of MDC, PBA and BDO were 98%, 92% and 93%, respectively. Consequently, the utilization of supercritical methanol in TPU degradation and recycle was efficient and promising.

2 Experimental

2.1 Material and equipment

Figure 1. Schematic diagram of the experimental equipment
1.High pressure reactor 2. Insulating layer 3. Salt bath
4. Thermostat 5. Resistance wire
6. Stiring 7. Vacuum pump 8. Thermocouple
9. Temperature display instrument 10. Pressure transmitter

The polyurethane which was decomposed in this research was thermoplastic polyurethane elastomer (TPU): Bayer

Desmopan® CA205; The solvent was absolute methanol(AR,purity≥99.5%). The experimental apparatus is shown as Fig. 1, it was a high pressure batch reactor with a volume of 20ml made of 316L stainless steel. The reactor was heated by molten salts which contained 50wt.%KNO₃ and 50wt.%NaNO₂. The volume of the part exposed to the air is less than 0.1ml, so the affection of the unheated part to the whole system could be ignored. The temperature and pressure in the reactor were measured by pressure sensor and K-thermocouple, respectively.

2.2 Experiment and characterization

2.2.1 The feasibility of TPU degradation in supercritical methanol

1.0000g±0.0002g of raw TPU was weighed by electronic balance and fed into the above-mentioned high pressure batch reactor. The degradation condition was set as 250 °C /9.0MPa. The reactor was sealed up and vacuumized to -0.01Mpa by water ring vacuum pump. 12.5ml of methanol(the mass ratio of raw TPU and methanol is 1:10) was extracted by needle tubing and inhaled by the negative pressure. Then the reactor was heated by the melting salt. After 20min, the reaction was finished, the reactor was taken out of the molten salt and put into cold water immediately. When the temperature of the reactor reduced to ambient temperature, the degradation products were taken out and analyzed by GC-MS(GC: Agilent 6890, MS: Agilent 5973N).

In addition, A WRT-3P TG was used in testing 30mg of TPU in the atmosphere of N₂.

2.2.2 Degradation of TPU in sub-/supercritical methanol

The experimental procedure was the same as which was mentioned in 2.2.1. The degradation temperatures were in the range of 200~290 °C, the corresponding pressures were 3.0~13.0MPa. The duration of the degradation was 5min~70min.

Analytical instruments : Haixin GC-930, FID; Waters600 HPLC, Waters486 UV(246nm) ; JEOL JSM-6360LV scanning electron microscopy(SEM).

2.2.3 Characterization of PBA in suitable degradation condition

At 230 °C/7.2MPa, the degradation time was 5min~70min. After vacuum distillation, the products were dissolved in tetrahydrofuran(THF) and analyzed by GPC(PL-GPC50, mobile phase: THF) .

3 Results and discussion

3.1 The degradation results of supercritical methanol

The degradation products in supercritical methanol(250 °C /9.0MPa) were faint yellow liquid mixture. That indicated 20min was enough for supercritical methanol to degrade TPU completely. By contrast, TPU decomposition started at 300 °C and finished at 700 °C in thermolysis, as shown in Fig. 2. Therefore, supercritical methanol was superior to thermolysis on account of lower decomposition temperature and higher efficiency.

Figure 2. TG curve of TPU

Testing of the products mixture by GC/MS indicated that there were THF, BDO, dimethyl adipate (DMA), MDC, et al; Thereinto, THF was a byproduct from BDO cyclodehydration; A part of BDO was chain extender of TPU, the other was methanolysis product of PBA, as the same as BDO. GC was not proper to PBA which was a polymer itself. But from the methanolysis products of PBA, it could be inferred that the degradation products mixture also contained PBA.

3.2 Degradation of TPU in sub-/supercritical methanol

As the results shown above, the degradation products of TPU in supercritical methanol were MDC, BDO, PBA and its methanolysis products BDO, DMA. BDO and DMA were quantified by GC; MDC was quantified by HPLC [12]; PBA was measured by GPC. On the basis of these analyses, the influence of temperature and time on degradation rate and yields were obtained.

3.2.1 Analysis on degradation residue

The quality of the degradation residue was weighed and shown in Table 1. At 200 °C/70min, the quality of the residue was 0.5076g. In the range of 200 °C to 240 °C, the time of TPU decomposing completely was decreased significantly. When the temperature of the degradation was higher than 240 °C, the degradation reaction completed within 10min.

The SEM images of degradation residues in 200 °C to 250 °C, 10min were given as Fig. 3 to Fig. 9. There were plenty of micro areas on the surface of TPU, as shown in Fig. 3. Because TPU was a block copolymer consisting of hard segment and soft segment, hard segment was generated from MDI and chain extender, and could not be

dissolved in soft segment which was composed of PBA. The alternative distribution of the two kinds of segments formed micro areas. This phenomenon was called microphase separation. In 200°C~210°C, the methanol molecule firstly infiltrated the amorphous soft segment. The polymer chains were decomposed to oligomers. As Fig. 4~Fig. 5 showed, the TPU fragments with microphase separation were observed. At 220 °C, as shown in Fig. 6, the fragments continued to react with methanol, part of soft segment was dissolved in

methanol, deprived from the polymer chains, the others twined around the hard segment. In Fig. 7~Fig. 8, the degradation temperature rising to 230°C~240°C, all the soft segments had removed from the TPU chains. Some of them attached to the hard segments which were spherical crystal arranged closely. At 250 °C /10min, supercritical methanol diffused into TPU, and the soft segments were rapidly ruptured from TPU. The internal structure of hard segments rearranged and congregated into flake-shaped fragment, as shown in Fig. 9.

Table 1. Quality of the degradation residue

Degradation time/min	Quality of the degradation residue/g									
	200°C	210°C	220°C	230°C	240°C	250°C	260°C	270°C	280°C	290°C
10	0.8084	0.7718	0.6043	0.3045	0.103	0.0173	0	0	0	0
20	0.7777	0.6812	0.4678	0.23	0	0	0	0	0	0
30	0.7323	0.5343	0.3291	0.1	0	0	0	0	0	0
40	0.6372	0.5025	0.1962	0.05	0	0	0	0	0	0
50	0.5769	0.3928	0.1433	0	0	0	0	0	0	0
60	0.5934	0.28	0.0827	0	0	0	0	0	0	0
70	0.5076	0.1514	0.0367	0	0	0	0	0	0	0

Figure 3. SEM image of TPU surface

Figure 5. SEM image of the degradation residue at 210°C /10min

Figure 4. SEM image of the degradation residue at 200°C /10min

Figure 6. SEM image of the degradation residue at 220°C /10min

Figure 7. SEM image of the degradation residue at 230°C /10min

Figure 8. SEM image of the degradation residue at 240°C /10min

Figure 9. SEM image of the degradation residue at 250°C /10min

3.2.2 Analysis of the degradation products mixture

During the main products of the depolymerization, BDO, DMA were measured by GC internal standard method with naphthalene as the internal standard substance. While MDC had high boiling points, and would

decompose above 200 °C . GC method was not appropriate.

To ensure the isocyanate(NCO^{''}) reacting entirely, the products needed to be treated with excessive methanol before measuring by HPLC external standard method.

Figure 10. Relationship between yields of MDC and temperature

Figure 11. Relationship between yields of DMA and temperature

The influences of temperature and time on the main products MDC were represented in Fig. 10. In the temperature of 200~230°C, the yield of MDC increased with the temperature. In 240~260°C, the yield of MDC exhibited apparent peak values which showed earlier with increasing temperatures. On account of the secondary reaction above 250°C[12], the yield of MDC reduced sharply. The maximum yield of MDC reached 98% at 230°C /70min. Higher temperature was not good for MDC recycling.

DMA and part of BDO were decomposed from PBA. The yield of DMA was low(approximate 5%) below 230°C

as represented in Fig. 11. So that the PBA was rarely broken down below 230°C. In addition, the yield of the chain extender BDO could reach to 93% (Fig. 12). To sum up, in subcritical methanol(230 °C /7.2MPa), the yields of MDC and BDO were high, and the decomposition rate of PBA was low.

Figure 12. Relationship between yield of extender(BDO) and degradation time

3.2.3 Characterization of PBA

According to the study in 3.2.1 and 3.2.2, 230 °C /7.2MPa was the appropriate condition of TPU degradation in methanol. But one of the main products PBA was polymer, it needed to be measured by GPC.

Figure 13. Molecular weight distribution of degradation products in 230 °C/20min

The molecular weight distributions (MWDs) of the products mixture at 230 °C were analyzed by GPC. Take the MWD at 20min as an example, as represented in Fig. 13, the peak of PBA could be separated from the monomer peaks by origin8.5 PFM. The MWDs of PBA at different times were shown in Fig. 14. The molar

concentrations of PBA were also obtained by calculation (Fig. 15). The maximum yield was 92%.

Figure 14. Relationship between MWD of PBA and degradation time

Figure 15. Relationship between yield of PBA and degradation time

4 Conclusions

Our research realized that supercritical methanol performed excellently in TPU degradation. TPU decomposed efficiently to obtain its raw material MDC, PBA and chain extender BDO. In the optimum degradation condition 230 °C /7.2MPa, the yields of TPU MDC, PBA, BDO could reach 98%, 92% and 93%, respectively.

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