Microwave Synthesis Of Polyols For Urethane Materials

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Abstract. The preparation of polyurethane (PU) polyols processed with the use of microwave (MW) irradiation heating polyols is reported. The PU polyols were consisted from bio-based rapeseed oil (RO) and recycled polyethylene terephthalate (PET) components are reported. Obtained MW polyols were compared to the conventional PU polyols synthesized by traditional heating in oil bath. The polyols have the similar properties. The obtained MW assisted polyols were characterized by Fourier transform infrared spectroscopy (FT-IR) measurements. Acid number, hydroxyl value, moisture content and viscosity of the MW synthesized polyols were measured. The obtained polyols consisted from about 34% RO and 23% PET components. The advantages of the very fast reaction rate for preparation of PU polyols, by using MW instead of the conventional heating process, are shown.

1. Introduction

All types of thermally driven chemical reactions can be accelerated by the use of microwaves (MW). From the early 1980-ties, many investigations have been performed in the field of MW synthesis of different organic substances. It is possible to decrease significantly the synthesis reaction time from hours to minutes. Arrhenius equation (1) testifies that very low activation energy should be applied to start the chemical reaction [1].

$$k = Ae^{-E_a/RT}$$  

(1)

Recently, natural raw components for polyurethane (PU) preparation have attracted considerable interest because of the environmental concerns [2]. Rapeseed oil (RO) can be chosen as bio-based and renewable feedstock to produce polyol components for PU materials manufacturing [3]. RO does not contain necessary hydroxyl groups and cannot react with the isocyanate components, but it can be chemically converted to the PU polyol. For the chemical modification are used reactions of ozonolysis [4], epoxidation [5], hydroformylation [6], esterification [7] and amidization [8]. The utilization of recycled polyethylene terephthalate (PET) for production of PU, has become very popular in the last years [9]. The depolymerization products of PET can be successfully utilized in the production of PU polyester polyols, which are also successfully used for preparation of the PU foams [10]. The glycerol (GL) and adipic acid (ADA) are generally used to improve the branching and functionality of the polyol [11]. Researchers also
report that MW irradiation can be utilized for the PET depolymerization and further preparation of the PU polyols [12, 13].

The main aim of the present paper is connected with synthesis of polyols for urethane materials preparations. The synthesized PU polyols consisted from renewable and recycled components. The clear PET bottle waste was depolymerized by the glycolysis reaction with diethylene glycol (DEG) under MW irradiation conditions. The MW polyols were compared with conventionally prepared polyols. The results of the both synthesis technologies were compared and discussed.

2. Experimental

The MW assisted synthesis was accomplished on the lab. scale 1-liter full glass reactor equipped with MW generator, mechanical stirrer, argon flux and condenser. The photo of the experimental laboratory glass reactor equipped with MW generator is shown in Fig.1. The MW generator frequency was 2450 MHz, power – 800 W. Considering the precise temperature control of the reaction bulk, the applied power for the synthesis was only 60%.

PET flakes of clear grade were granted from PET Baltija, Latvia. RO (I$_2$ = 117 I$_2$ mg/100 g) was supplied from Iecavnieks &Co, Latvia. The three different polyols were prepared with MW assisted synthesis process. The first MW polyol was RO/TEA, synthesized at 170 °C; RO and TEA molar ration was 1 M: 2.9 M. The second polyol was RO/PET. After the synthesis of RO/TEA, the 2 M of the recycled PET flakes and DEG were introduced to the reaction mixture. The temperature was increased up to 230 - 240 °C; reaction time was about 40 min. The third polyol was similar to the second, but GL and ADA additives were introduced to the reaction mixture to enhance the functionality of the product. GL and ADA content was equal to 1 wt.%.

For the comparison purposes, the same polyols were also prepared at 170– 240 °C in an oil bath, under argon flux and with mechanical stirrer. The content of the raw components for this series was the same as for the MW synthesis.

The Fourier transform infra-red spectra measurements (FTIR) were performed for chemical structure identification. The FTIR measurements were made on a Perkin-Elmer spectrometer Spectrum One FTIR Spectrometer.

3. Results and discussions

At the beginning, the advantages of the MW heating technology application under the conventional heating process can be defined by the investigation of the synthesis processes time kinetics. MW assisted synthesis process of PU polyols was compared with the same PU polyol prepared with conventional heating process. Table 1 has summarized the synthesis time parameters and characteristic properties of the processed polyols.

The three parameters were used to characterize the process kinetics: $t_1$ – time when the necessary synthesis temperature is achieved (relating to the process, the temperature was 170 and 240 °C); $t_2$ – time when homogeneous mixture is achieved; $t_3$ – synthesis full time. It should be stressed that the necessary temperature to start PET glycolysis and polyol synthesis reaction can be achieved after 2-4 minutes of MW irradiation heating. For the conventional process $t_1$ was about 2-3 hours for all polyols. The average MW synthesis full time $t_3$ for the polyols was about 6 minutes for RO/TEA, and about 40 minutes for RO/PET and
RO/ADA/GL polyols. It is clear that the MW process rate were significantly higher, than, conventional heating synthesis of the same polyols. Depending from the polyol, the MW process time was about 4-40 minutes consuming much lower energy, than conventional electrical heating, which was about 2-3 hours. More rapid MW heating is connected with high dipole moments of the used raw molecules [1]. In the conventional process, the reaction mixture is in contact with the reactor glass walls, which are heated first with the use of conducting medium. Then heat conductance through the oil medium is of very low efficiency [5]. This can be used to explain the difference between the rates of the two heating processes.

![Fig.1. Experimental MW assisted laboratory synthesis facility](image-url)

The obtained polyols' OH values are from 350 till 400 mg KOH/g. All processed polyols have low acid numbers, which are less than 7 mg KOH/g. The received values are suitable for the production of rigid PU foams. Water content in all polyols is less than 0.35% which is also acceptable for obtaining the PU foams.

The PU polyols synthesis has led to the formation of a viscous liquids, which did not solidify on cooling. The color of the polyols was from yellow to brown. The color of the polyols does not depend from the applied heating technology. The MW assisted polyols’ viscosity, reported in Table 1, was in the range from 160 to 1250 mPas for both polyols series. The polyols RO/TEA is characterized as a low molecular compound [8]. RO/PET and RO/ADA/GL polyols are more oligomeric [14]. GL/ADA addition in the synthesis modifies the chemical structure of the polyol and decreases the viscosity of the polyol. The obtained viscosity values are also appropriate for manufacture of the PU foams [15].
Table 1. Property comparison of MW assisted synthesis polyols with conventional process polyols

| No | Property          | MW assisted polyols | Conventionally heated polyols |
|----|-------------------|---------------------|-------------------------------|
|    |                   | RO/TEA;             | RO/PET | RO/GL/ADA | RO/TEA; | RO/PET | RO/GL/ADA |
|    |                   | RO/PET | RO/GL/ADA |            | RO/TEA; | RO/PET | RO/GL/ADA |
| 1  | t₁, min           | 2       | 4         | 4          | 120     | 235    | 75       |
| 2  | t₂, min           | 6       | 40        | 40         | 60      | 60     | 75       |
| 3  | t₃, min           | 6       | 50        | 90         | 120     | 120    | 135      |
| 4  | Color             | yellow  | brown     | brown      | yellow  | brown  | brown    |
| 5  | Hydroxyl number,  | 360     | 348       | 408        | 363     | 235    | 407      |
|    | mgKOH/g           |         |           |            |         |        |          |
| 6  | Acid number,      | n.a.    | 6.5       | 3.9        | 2.5     | 3.2    | 4.2      |
|    | mgKOH/g           |         |           |            |         |        |          |
| 7  | Viscosity,        | n.a.    | 810       | 630        | 160     | 1250   | 725      |
|    | mPa s             |         |           |            |         |        |          |
| 8  | Water content,    | 0.19    | 0.36      | 0.12       | 0.12    | 0.32   | 0.14     |
|    | wt.%              |         |           |            |         |        |          |

Fig. 2. FTIR-ATR spectra for MW assisted polyols RO/PET, RO/GL/ADA, and RO/TEA
The obtained FTIR spectra of the polyols prepared by the both heating technologies are very similar. The FTIR spectra of the MW process are presented in Fig. 2. The spectra of RO/TEA is similar to the previously discussed in the literature [16]. The spectra of the MW synthesized RO/PET and RO/GL/ADA polyols confirmed the PET glycolysis with DEG. FTIR spectra testified very close chemical structure of the polyols. The presence of recycled PET component in the polyol is mainly indicated by the absorption band intensities of aromatic C=C vibrations at 1578, 1505 and 1410 cm\(^{-1}\), the absorption band of bending and stretching vibrations of aromatic C–H at 875 and 730 cm\(^{-1}\) and the stretching vibration band of aromatic C–O carbonyl group at 1265 and 1120 cm\(^{-1}\). The broad band at 3400 cm\(^{-1}\) characterizes the free hydroxyl –OH groups in all polyols. There is also an important absorption band at 1710 cm\(^{-1}\), which corresponds to the carbonyl C=O bonds in ester groups.

It should be also mentioned that the synthesized polyols consisted from 34% renewable (RO) and 23% recycled (PET) components; they combined the advantages of aromatic and aliphatic structure blocks in the molecule backbone. Additionally, it can be noted that the rigid PU foams preparation was also tested in the lab. The MW obtained polyols were mixed with different additives to obtain general-purpose polyol compositions, which are suitable for preparation of rigid PU foams with thermal insulation properties. The PU foams prepared from MW assisted polyols have very similar structure and properties to the PU foams processed from conventional ones.

4. Conclusions

The utilization of MW for synthesis of PU polyols was testified experimentally in the lab. MW polyols have the similar properties as the traditionally synthesized polyols. Microwave assisted synthesis took place at extremely higher rates as compared to the conventional oil bath heating technology. Acid number, hydroxyl value, moisture content and viscosity of the MW polyols have appropriate values to prepare rigid PU foams. The synthesized PU polyols consisted from about 34% renewable (RO) and 23% recycled (PET) components.

5. References

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