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Glycerin as a new glycolysing agent for chemical recycling of cold cure polyurethane foam wastes in "split-phase" condition

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Summary

In this communication, "Split-Phase" glycolysis of isocyanate derived cold cure foams, with glycerin as a new glycolysing agent, is reported. The process was simple and economically attractive among material recycling processes. Glycerin was used as a destroying solvent and sodium hydroxide as the catalyst, respectively. In order to study the ability of glycerin as a glycolysing agent and for selecting a system to obtain high quality recovered polyol, the effects of various reaction times were investigated and the characterization and comparison of upper and lower phases were performed by using instrumental (FT-IR, ^{1}HNMR and ^{13}CNMR) and classical methods.

Keywords

Glycerin; Glycolysis; Polyurethane waste; Recycling; Flexible PU foam, "Split-Phase"

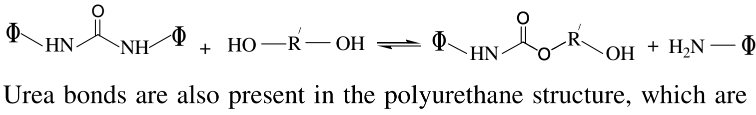
Introduction

During recent years the subject of polyurethanes (PU) recycling has been targeted, especially flexible PU foams, due to extensive PU applications, high volume of wastes and also with a view to solving environmental and economic problems. PU cold cure foams, which are the most important group of foams, constitute 29% of total production of these materials. These foams are widely are used in furniture, mattresses and automotive seats [1]. Current methods for recycling include processes such as granulating scrap for the manufacture of rebounded flexible foam [2], cryogenic pulverization to powder particles for use as a filler [3], hydrolysis [4,5], aminolysis [6], pyrolysis [7,8] and glycolysis. Among the latter named methods, the glycolysis process for converting waste back to starting raw materials has special importance.

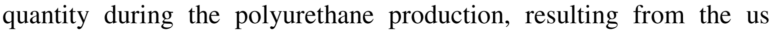
A chemical recycling process for flexible PU, based on "Split-Phase" glycolysis, has the capability to produce high quality flexible polyol that can be reused to make PU foam with a high recycled content. The "split-phase" glycolysis technique has been targeted to recover flexible polyol in high quality and consistency to replace virgin polyol. The process is particularly well-suited to the flexible foam slab stock markets where the volumes of production waste are sufficiently high to enable favorable economics [9].

Some studies have revealed that a proper glycolysis process may be used to resolve the disposal problems of PU wastes, along with obtaining a high quality polyol [9-12]. Simioni and Modesti investigated the glycolysis products of flexible PU foams at 190°C [13]. They used ethylene glycol (EG) as a glycolysing agent, with process performed with high polymer /glycol ratio (up to 4:1). The obtained polymeric product has been used for preparation of reaction injection molding PU. Kanaya and Takahashi [9] reported the decomposition of flexible PU foam by alkanol amines without a catalyst at 150°C [6]. The decomposition products were completely separated in to two layers. In this report, according to the chemical structure of the alkanol amine derivatives, it was assumed that the decomposition reaction of urethane foam by monoethanolamine (MEA) takes placed via an alcoholysis reaction. In other words, the decomposition reaction begins with the association of MEA and the urethane group. Modesti and his co-workers carried out the glycolysis of flexible PU foams in the presence of EG and an organometalic catalyst [14]. Borda and his co-workers investigated the glycolysis of flexible PU foams and elastomers in the temperature ranges of 170-180°C [15]. The reagents used were EG, 1, 2-propylene glycol, triethylene glycol, polyethylene glycol and diethanolamine. In this study, a reaction mechanism was proposed for the glycolysis of polyurethanes. The polyol component, which was separated from two liquid phases, could be used as an industrial adhesive. Troev and his co-workers investigated the chemical degradation of flexible PU foams by triethyl phosphate [16]. The degradation temperature was 190°C and the results indicated that the flexible PU foams could be converted into liquid form by an exchange reaction between the urethane group and ethoxy groups of phosphoric acid triethyl ester. On the other hand, the obtained products were phosphorus containing oligourethanes. Chao-Hsiung used high temperature (220 ± 5°C) condition to investigate the glycolysis reaction of flexible PU from wastes car seats [17]. Diethylene glycol (DEG) and potassium acetate (KAc) were utilized as solvent and catalyst, respectively. They studied the effect of the reaction time and the DEG and KAc concentrations on the properties of the glycolysed product. Rodriguez *et al.* investigated two-phase glycolysis reactions of flexible PU foams based in polyether polyols with different low molecular weight glycols, such as monoethylene glycol (MEG), diethylene glycol (DEG), 1, 2-propylene glycol (MPG) and dipropylene glycol (DPG), in order to obtain recycled polyol [18]. In this study, reaction kinetics and products obtained were investigated and also diethylene glycol proved to be the most suitable glycol to obtain a high purity polyol.

The chemistry of glycolysis involving the break down of the urethane bonds, in which the polymer chain is decomposed to a mixture of liquid oligomers, proceeds according to the following reactions (eq. 1 and 2) [19]:

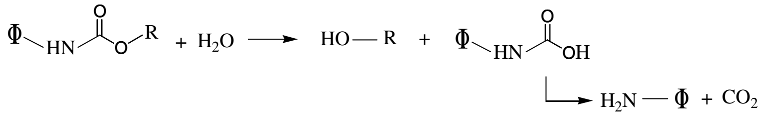


(1)



(2)

Urea bonds are also present in the polyurethane structure, which are formed in small quantity during the polyurethane production, resulting from the use of water as a foaming agent. Therefore the hydrolysis reactions can lead to the evolution of CO_2 and to the formation of amine groups (eq. 3) [18]:



(3)

Transesterification reactions involving the urea and urethane bonds and decarboxylation reactions lead to a variety of by-products, which can be increased due to pyrolysis reactions at the glycolysis temperature.

In the continuation of our previous experiments involving the glycolysing of PU wastes, we decided to examine the ability of glycerin as a glycolysing agent for recovery of high quality polyol from cold cure foams [20, 21]. To eliminate the amine catalysts we used glycerin alone, seeking to obtain optimum conditions. Thus, the glycolysis reaction was performed in various reaction times and conditions. In our knowledge, we report for the first time glycolysis of PU using glycerin.

Experimental

Materials and instruments

Industrial samples of flexible cold cure PU foam, which was derived from non recycled (virgin) polyol Daltoflex EC 20240, was used. The formulation consisted of activated polyether polyols, aliphatic amines catalysts, surfactant and water. The polyol was a colorless viscous liquid, having a viscosity of 1.250 Pa.s at 20ºC, specific gravity of 1.035 $g.cm^{-3}$ at 20ºC, fire point 240ºC (Mw ~ 1900, functionality 2 and hydroxyl number of 59 mg KOH/g) and in combination with Suprasec 2027 diphenylmethanediisocyanate (MDI) based prepolymer. The MDI was a dark brown liquid, having viscosity of 0.220 Pa.s at 25ºC, specific gravity 1.23 $g.cm^{-3}$ at 25ºC, NCO value of 30.9 % by wt NCO groups analysis (group weight : 42 $g.mol^{-1}$, average functionality 2.7, flash point 233 ºC, fire point 245ºC). Daltoflex EC 20240 and Suprasec 2027 are chlorofluorocarbon (CFC) free systems, purchased from HUNTSMAN® Company with starting formulation as (Daltoflex EC 20240: 100 *pbw*, Suprasec 2027: 65 *pbw*, recommended mold temperature: 40-45ºC; demolding time 5 min.; molding density: 42-47 $kg.m^{-3}$). The prefix “VIRGIN” is used in order to differentiate the non recycled polyol from the recycled polyol.

FT-IR, ^{1}HNMR and ^{13}CNMR spectroscopic methods were used for characterization of recycled products and comparisons with virgin one. FT-IR spectra were done by using a BRUKER Tensor 27 spectrometer (droplet samples were impregnated on KBr pellets). ^{1}HNMR and ^{13}CNMR spectra were done using a BRUKER CRX 300 instrument by using $CDCl_3$ as a solvent. Hydroxyl numbers (OH No.) were determined by using JEOL JNM-EX 90A NMR instrument according to the ASTM D 4273-94 method.

Molecular weight distributions were determined by using 6A SHIMIDZU gel permeation chromatography (GPC) instrument at column type: BRUKER PL gel 5 µ, 1000 Aº, column length 30 cm, mobile phase: tetrahyrofuran (THF), temperature: 40ºC, flow rate: 1 $cm^{3}.min^{-1}$, injection volume: 100 µL, calibration: polystyrene standards (950, 2200, 5100, 11600 Mw’s), detection: RI (Refractive Index) conditions. Viscosities were determined using HAAKE viscometer.

General procedure of glycolysis process

A 3-necked round bottom flask was used for process. The flask was equipped with a mechanical stirrer and a removable reflux condenser. The mixture of glycerin (125 g) and NaOH (1.25 g) preheated until a homogenous solution is obtained. PU foam wastes (125 g) which were segmented in arbitrary diameter ranging from 5 to 15 mm were added gradually to the reaction mixture at temperature ranges of 170-190°C at 30 min. Transesterification reaction carried out at atmospheric pressure. The reaction extends to complete dissolution of foams. Reaction mixture was sampled at 30, 60, 90, 120, 150 and 180 min intervals, transferred to a decanted funnel and was left to be cooled in room temperature. After several hours it was separated into clear yellow upper and dark brown lower phases. The separated phases were analyzed by classical and instrumental methods.

Results and discussions

In order to reducing the amine content of recycled products, glycerin were selected as glycolysing agent and NaOH as a catalyst and experiments were followed in the absence of amine decomposer. In a typical experiment, tri-phases are obtained. The upper one constituted mainly by the recovered polyol and the bottom one formed by transesterification by-products and the excess of glycerin. The third phase is formed in a low amount (<10 parts by weight of the whole glycolysis products) located between the upper phase and the lower one, having a semisolid state (gelatinous) containing a mixture of worthless materials that wasn't characterized.

Figure 1 show GPC chromatograms of sampled upper phases at different reaction times.

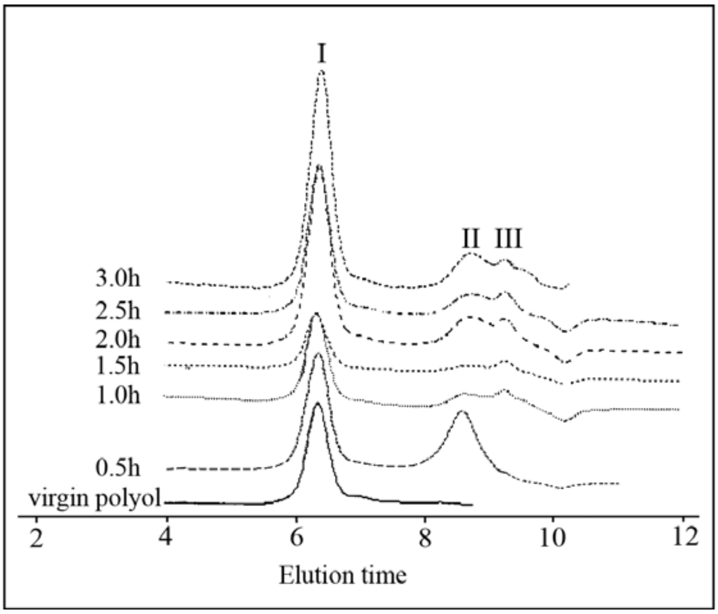


Fig. 1. GPC chromatograms of virgin and recycled polyols in different sampling times I: polyol, II: transesterification by-products and III: glycerin

Peak I corresponded to the recovered starting polyol. The glycolysis reaction was progressed well into starting materials (polyol) by glycerin action that lead to break down of the polyurethane chains into smaller fragments and finally complete degradation of PU functional groups. The transesterification by-products formed by the substitution of polyol by glycerin molecules (peak II). The intensity of this peak in the chromatogram corresponded to 0.5h in comparison with the others is strong and wide. This show after a brief interval of perfect foams dissolution, phase separation could not take place completely. Therefore there is more amount quantity of the lower phase products in the upper one. Peak III, corresponded to the glycerin, which remained slightly in the upper phase. In Figure 2 (a) are shown the GPC chromatograms of the industrial starting polyether polyol used for the foam preparation and the reaction products obtained after complete decomposition of the PU.

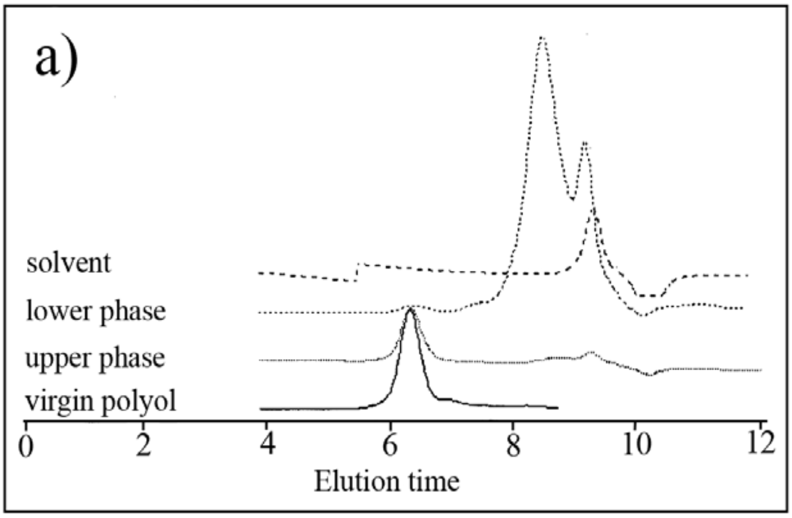


Fig. 2 (a). GPC chromatograms of "split- phases" and their elution time's comparison with virgin polyol

According to the results obtained from GPC chromatograms, the starting polyol is recovered completely which is the major product in the upper phase with similar elution times and characteristics to the virgin one. On the other hand, the presence of peaks II and III in the recovered polyol chromatograms in the upper phase shows the product pollution with bottom liquid layer having the low molecular weight because of very slight miscibility. In Figure 2 (b) are shown the chromatograms obtained for the bottom liquid phase and virgin polyol.

Lower phase was enriched by high polar products, mainly the excess of glycerin and aromatic by-products derived from the starting isocyanates. Although a little quantity of the lower phase is dissolved in the upper one, cause in decrement of its purity. The chromatogram of the bottom phase obtained with glycerin shows the characteristic peak of polyol (I), slightly. In Figure 3 are shown the FT-IR spectrum of the virgin polyol used in the preparation of the polyurethane foam (a) and upper phase after 1h (b) and 3h (c) from perfect foam dissolution.

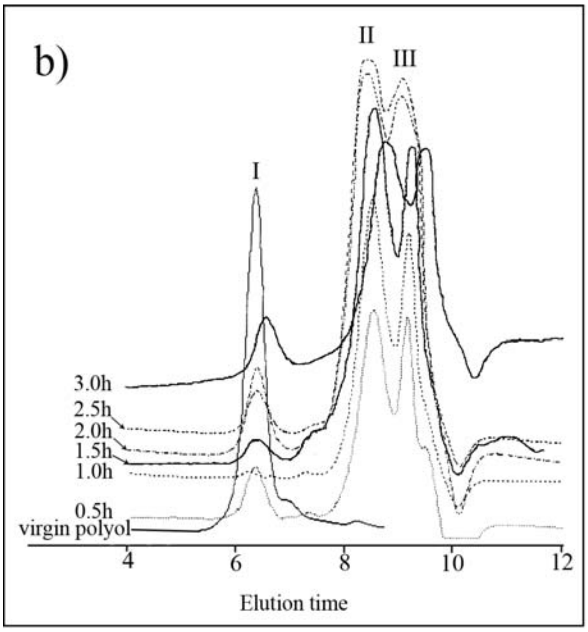


Fig. 2 (b). GPC chromatograms of virgin polyol and lower phase products at various reaction times

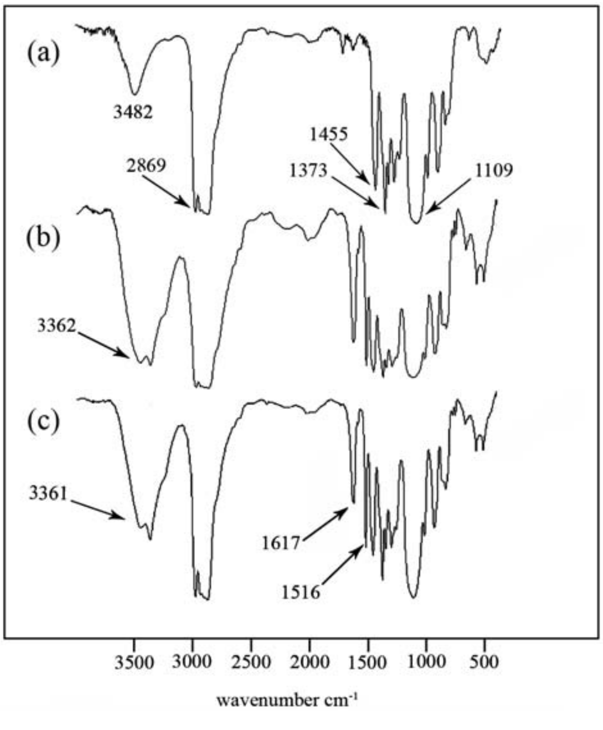


Fig. 3. IR spectra comparisons of: virgin polyol (a), recycled polyol, after 1h (b) and 3h (c) from perfect foam dissolution

The peak in the spectral region of 1109 cm^{-1} corresponded to stretching vibrations of the aliphatic ether groups together with the bond produced by CO groups associated to hydroxyl end groups as overlapping and stretching vibrations of these OH groups at 3482 cm^{-1}. The later band has been broader in (b) and (c) in comparison with virgin one (a) probably, due to presence of primary amine contaminants (eq. 2 and 3) in upper phase. The absorption bands in the spectral region of 2869-3000 cm^{-1} are corresponding to stretching vibrations of CH bonds in aliphatic carbons and in 1455 and 1373 cm^{-1} characteristic of bending vibrations of methylene and methyl groups in the polyol chain [18]. The comparison of the IR spectra of virgin and recyclated polyols shows the structural similarity of them. There are only a few slight differences between virgin and recovered polyols. One the absorption bands at >3000 cm^{-1} in (b) and (c) are widened by the presence NH groups in the upper phase as contaminant (the absorption bands at 3362 and 3361 cm^{-1} in (b) and (c) respectively) and another the presence of new absorption bands at 1617 and 1516 cm^{-1}, in (b) and (c) spectra that related to the bending vibrations on amine group that slightly has been dissolved in upper phase. Although glycerin is dissolved in the upper phase in small amount, since all stretching vibrations of glycerin bonds (C-O and OH bonds) locate in the same spectral regions that C-O and OH bonds of starting polyol appears in IR spectra. Therefore it is not caused observable changes in absorption bands except the increasing in the quantity of hydroxyl groups that lead to increasing in the intensity of absorption bands at 3362 and 3361 cm^{-1} in (b) and (c) respectively.

Bond assigned to the stretching vibrations of the carbonyl groups in urethane linkage are found in the 1690-1749 cm^{-1} [22-24]. Since no absorption band has been found in these regions in (b) and (c) spectra, revealed the completion of the urethane bond broking at 1h after perfect dissolution of the foam.

For more evaluation, ^{1}HNMR and ^{13}CNMR spectra of virgin and recycled polyols were investigated. Figure 4 shows ^{1}HNMR (a) and ^{13}CNMR (b) spectra of virgin polyol, respectively.

Most of the bonds assignments in ^{13}CNMR spectrum have been indicated [25]. In ^{1}HNMR spectrum, the peak in the region 1.1 ppm is corresponding to methyl equivalent hydrogen's and the peaks in the 3.0-4.0 ppm are relative to hydrogen's that their carbons directly connected to the oxygen [26]. The comparison of ^{1}HNMR spectra of virgin polyol and recycled product in the upper phase (Figures 5) represents that chemical structures of these compounds are too similar, except the peaks in the region about 6.6-7.1 ppm and 6.9-7.2 ppm in Figs. 5(b) and (c) respectively, are corresponding to aromatic ring hydrogens derived from the aromatic diamines which partially have remained in the recovered polyol. Also only deference between ^{13}CNMR spectra of recovered polyols and virgin one (Figure 6) is the presence of the signals in low peak area about 110-140 ppm in ^{13}CNMR spectra of recycled polyols that originated from the starting isocyanats as contaminant.

Figure 7 shows IR spectrum of the lower phase that containing the mixture of carbamate, urea, decarboxylated products and excess glycerin. The absorption bonds in the spectral regions 3418, 1614 and 1516 cm^{-1} in high intensity, confirm the presence of urea, carbamate and similar functional groups in the lower phase in higher concentration than the upper one. Comparison of (a) and (b) spectra, represents no significant reactions after 1h to 3h from perfect dissolution of PU. So the obtained products in specified intervals are quite equal.

The obtained results from GPC, NMR and IR confirm complete degradation of urethane chains at 1h after perfect foam dissolution. But for the gaining of reassurance

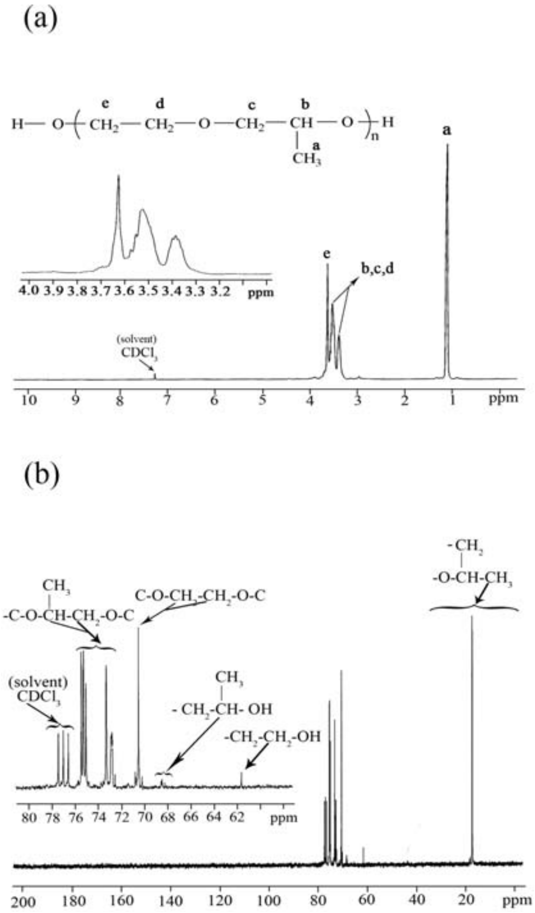


Fig. 4. ^{1}HNMR (a) and ^{13}CNMR (b) spectra of virgin polyol

of reaction completion, the reaction went on until 3h. The obtained results indicated with reaction progress after 1h, no noticeable change is observed in the glycolysis products and/or in the upper/lower phase ratio. This fact shows the susceptibility of glycerin together with sodium hydroxide as a strong destroying agent in degradation of urethane chains in a short time after perfect foam dissolution.

Another method for the comparison of recycled and non recycled polyols was hydroxyl number (OH. No.) determination. According to ASTM D 4273-94 by ^{13}CNMR method, polyol (0.6 g) was dissolved in $CDCl_3$ (0.4 g) as solvent (sample/solvent ratio 3:2), thoroughly mixed and were added to the NMR tube. A sufficient number of repetitive of pulses were accumulated by using NMR 90 MHz spectrometer until the peaks of the primary and secondary hydroxyl carbons can be accurately measured by the spectrometer's integration system. The mentioned peaks appear in the spectral region between 60-68 ppm in ^{13}CNMR spectrum that previously was assigned in figure 4 (B). As shown in figure 8, ^{13}CNMR spectra of virgin (a) and recycled polyols after 1h (b) and 3h (c), from perfect foam dissolution were expanded, amplified and integrated for determination of hydroxyl numbers.

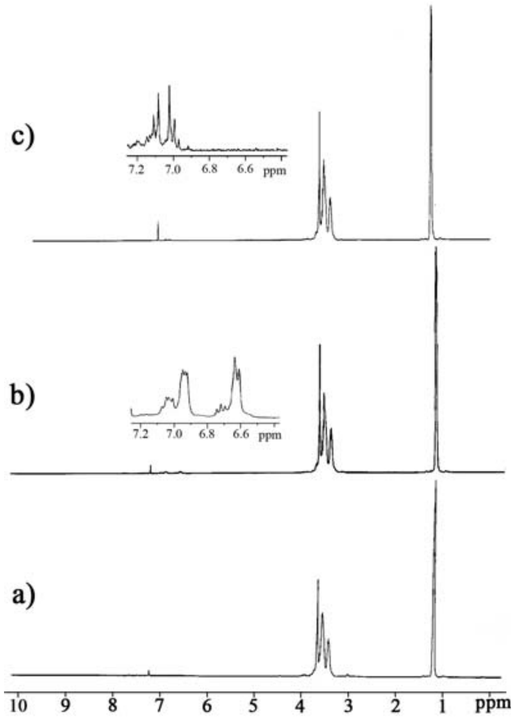


Fig. 5. ^{1}HNMR spectra of virgin (a) and recycled polyols after 1h (b) and 3h (c) from perfect foam dissolution

Since the peaks of the primary and secondary hydroxyl carbons relative to remained glycerin in the recycled polyol, appear in the spectral region 58-68 ppm, the later region in Figurs 8 (b) and (c) is more crowded that presumably some of them have overlapped.

% OH for any sample was calculated according to eq. 4 [27]:

$$\%\,\mathrm{OH} = \frac{\begin{array}{c}\text{Area of primary hydroxyl peaks}\\ +\ \text{Area of secondary hydroxyl peaks}\end{array}}{\text{Area of all peaks in the spectrum}} \times 100 \qquad \textbf{(4)}$$

And,

$$\text{OH number} = \%\,\text{OH} \times 33 \qquad \textbf{(5)}$$

The hydroxyl numbers of recycled polyols are higher due to partial solubility of glycerin in the upper phase in comparison with virgin one (59 mg KOH g^{-1}). The hydroxyl values for the recycled polyols at 1h and 3h after perfect foam dissolution were determined, 99 and 73 mg KOH.g^{-1}, respectively. On the other hand, when the reaction progressed, the concentration of glycerin decreased in upper phase, causes decreasing in hydroxyl values. So the obtained polyol after 3h has less hydroxyl value than the polyol one after 1h.

Another observation in studied reactions was the CO2 evolution from reaction mixture. This process is concluded from mass losses in the reaction end point as well as gas bubbling in cold sodium hydroxide solution [15].

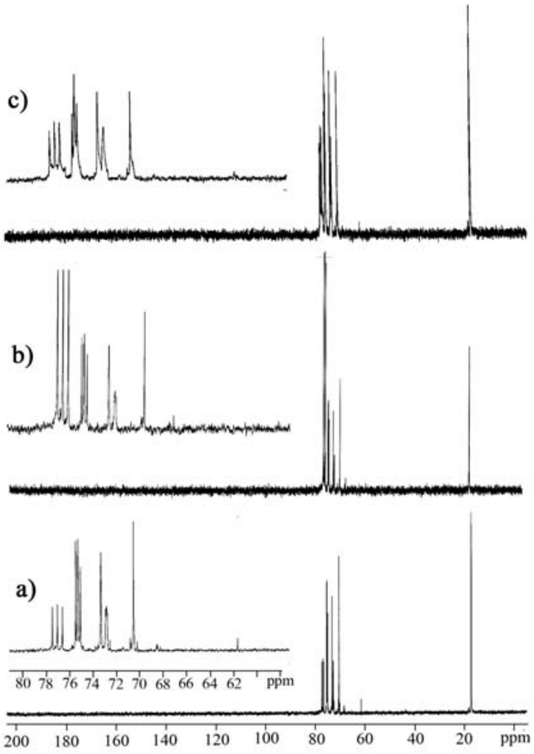


Fig. 6. Comparison of ^{13}CNMR spectra of virgin (a) and recycled polyol after 1h (b) and 3h (c) from perfect foam dissolution

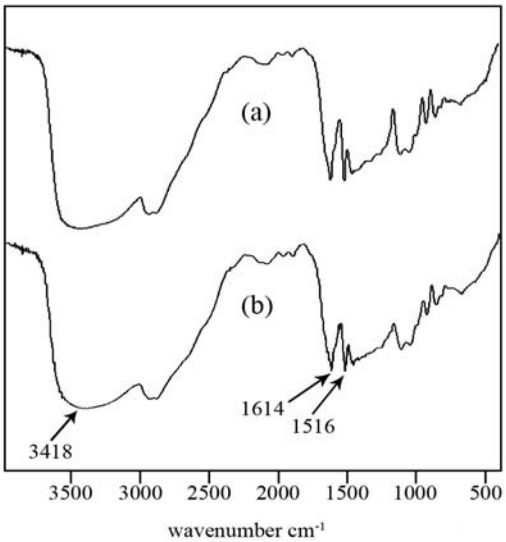


Fig. 7. IR spectra of lower phases: after 1h (a) and 3h (b) from perfect foam dissolution

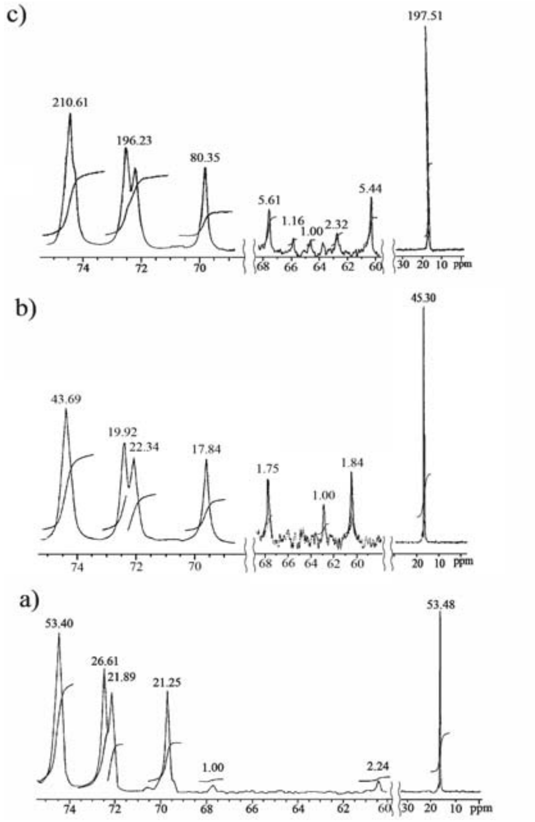


Fig. 8. ^{13}CNMR spectra of virgin (a) and recycled polyols after 1h (b) and 3h (c) from perfect foam dissolution for determination of OH Number

As polyol viscosity is the most physical parameter and influencing the PU foam injection. The viscosities of virgin and reaction mixture at various reaction times are shown in table 1. From table, the viscosity of Daltoflex EC 20240 is 1250 cPs, while reaction mixture has a maximum viscosity of 9600 cPs at 0.5 reaction time. On the other hand, viscosity decreased by increasing of reaction time due to successful polyurethane chain sessions. The obtained results from viscosity studies confirm GPC, NMR and IR data and showed complete degradation of urethane chains at 1h after perfect foam dissolution. On the other hand after 1.0 h there was any significant difference in viscosity.

Table 1: changes of viscosity of the reaction mixture versus time

Reaction time (h)	Reaction mixture viscosity (cPs)
0.5	9600
1.0	3560
1.5	3412
2.0	3425
2.5	3400
3.0	3450
Virgin polyol	1250

Conclusion

Glycolysis of cold cure PU foams has been investigated for recycling of starting polyol from PU wastes. The reaction was performed under atmospheric pressure in a stirred flask at temperature 170-190°C. Glycerin and NaOH were used as solvent and catalyst in the glycolysis system, respectively. The reaction was followed by using spectroscopic methods. Investigation of the obtained results from FT-IR spectroscopy indicates that chemical structure of recycled polyol after 1h and 3h are too similar to virgin polyol. Because the vibrations in the spectral regions >3300, 2869, 1455, 1373 and 1109 cm^{-1} in virgin polyol are repeated similarly in the recycled polyol. Except the vibrations at 1617 and 1516 cm^{-1} characteristic in the recycled polyol which are corresponding to the bending vibrations of amine N-H bands originated from the starting isocyanats as contaminant which slightly has been dissolved in the upper phase. Also ^{1}HNMR and ^{13}CNMR spectra of virgin and recycled polyols regardless the peaks about 6.6-7.2 ppm in ^{1}HNMR and the peaks in the region 110-140 ppm in ^{13}CNMR that are relative to the aromatic by-products, are quite equal. Also GPC results showed the similarity of recycled and virgin polyols. Another observation in our study was the higher hydroxyl value of recovered polyols in comparison with virgin one due to partial solubility of glycerin in the recycled polyol. According to the results, glycerin could be used as glycolysis agent to recovering of high quality polyol, which can be reused for production of new flexible PU foams. Also, the viscosity of the reaction mixture was decreased after 0.5 from foam dissolution and stay at constant value after 1 h.

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