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Rheological characteristics of oligomeric semi-products gained via chemical degradation of polyurethane foam using crude glycerin in the presence of different catalysts

Patrycja Kopczyńska[1], Janusz Datta[1*]

[1]Department of Polymer Technology, Faculty of Chemistry, Gdańsk University of Technology
G. Narutowicza Street 11/12. 80-233 Gdańsk, Poland
[*] Correspondence to: Janusz Datta (E-mail: jandatta@pg.gda.pl)

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Patrycja Kopczyńska, Janusz Datta

Abstract

Polyurethane (PU) recycling is a topic of growing interest due to the increasing amount of polyurethane waste. The main purpose of polyurethane chemical recycling is to recover the starting polyol. In this study, a method of polyurethane thermo-chemical recycling, glycerolysis by means of crude glycerin, is proposed. This work presents a comparative study of commercial catalysts used in order to accelerate the decomposition process, namely triethylamine (TEA), potassium acetate (KAc), 1,4-diazabicyclo[2.2.2]octane (DABCO), sodium hydroxide (NaOH), dibutyltin dilaurate (DbDl) and stannous octoate (StOc).The effect of used catalyst on the chemical structure and rheological properties was studied. The type of catalyst does not have significant influence on the chemical structure, but causes different course of reaction: split- and single-phase in applied conditions. Glycerolysates were measured by Brookfield Rheometer. It was found that re-polyols can be described by the Herschel-Bulkely mathematical model in the best accuracy. The investigation showed that the rheological behavior of glycerolysates depended on the catalyst used in glycerolysis process.

INTRODUCTION

Polyurethanes (PUs) make ca. 6% of total plastics production. The industrial consumption of polyurethanes increased due to technological developments and their use in new industrial applications, it is currently over 14 million tons. These polymers are valuable due to their various forms such as foams, coatings, adhesives, sealants, elastomers, (CASE) etc. therefore they have a wide range of applications in construction, automotive, freeze industry, furniture and medical industry. Polyurethane waste can be generated during the production of technical items as scraps or during post-production [1]. Only 58% of the polymer is recovered [2]. In the recent years, many researchers have focused their efforts on looking for solutions and new methods of polyurethane and plastic waste recycling to reduce the environmental impact of these materials [1][3][4]. Except landfilling, the incineration (energy recovery), mechanical and chemical recycling are known as the waste management ways. The recycling of plastic waste, apart from reducing the amount of waste, also helps to conserve natural resources as most polymeric materials are made from oil and gas [1][5]. The best-known methods of chemical recycling include: hydrolysis, glycolysis, alcoholysis, acidolysis and aminolysis [3].

In the above-mentioned methods of chemical recycling, the obtained semi-product is influenced not only by choice of decomposition reagent, but also by the type of used catalyst, which affects the time required to reach complete degradation and the reaction temperature. The importance of catalyst lies in the fact that, in contrast to direct esterification, trans-reaction with alcohol groups proceeds very slowly in the absence of catalysts under mild conditions [6]. Generally, catalysts are used in order to accelerate the decomposition reactions. The applied catalysts in polyurethane recycling include bases like amines, hydroxides, alkoxides and Lewis acids, leading to different extension in secondary reaction. Acetates of Pb, Zn, Ca, K, Na are described as general catalysts in the transesterification reaction, leading to high amine value in resulting semi-product [7] [8]. The utilized catalysts can steer going process for the benefit of recovering polyol or by-products. The catalysts can also promote a different types of reaction viz. single-phase and split-phase (two-phase) [9], [10] where the different resulting products (homogenous or two phase product) are obtained. Datta [11] and Murai et al.[12] proposed the mechanism of polyurethane glycolysis using KOH as catalyst. The KOH catalyst promotes a nucleophilic attack of an oxygen atom from the hydroxyl group of KOH on the urethane bond. This catalyst is not selective (as e.g. dibutyltin dilaurate) and during decomposition reaction simultaneously can go glycolysis and hydrolysis. As a result of the reaction between glycol and hydroxide, the salt and H_2O are formed. The hydrogen (from the –OH group of glycol) exchange causes a change in the nature of the chemical bond from polar covalent bond to ionic bond. When hydroxyl salt is near to polyurethane chain, a four-ring is formed, in which there are two bonds C-O and K-O. Statistically, one of the K-O bonds breaks and the reaction retreats with glycol hydroxyl salt reconstruction or the reaction proceeds to obtain the degradation products. Potassium salt is formed with the shorter rest of the polyurethane chain, which reacts with –OH group from glycol or water and KOH or $HO\text{-}R\text{-}O^-K^+$ and then a polyol terminated with the –OH group is created. The second reaction product is degraded polyurethane with a lower molecular weight, terminated with the glycol rest, used for glycolysis process. In Scheme 1, the described mechanism is shown according to use glycerin as decomposing agent.

It is known from the literature, that products of chemical recycling can be used to form new polyurethane material e.g. elastomers [13], [14] or foams [15]. This situation can take place as glycolysate can be similar to virgin polyol. Datta and Rohn [16] obtained glycosylates applied into polyurethanes synthesis as a component replacing partially or completely commercial polyol. PU elastomers indicated high tensile strength in range of 13.4/15.6 MPa and hardness in range of 85/94 °Sh A. Nikje et al. [17] used recycled polyol in foam synthesis, where re-polyol was mixed with the virgin polyol in amounts of 30, 40, 50 and 60%. Simon et al. [18] carried out glycolysis of polyurethane foam and utilized the obtained two-phase glycolysate in flexible and rigid polyurethane foams, from the upper and bottom phase, respectively.

Nonetheless many factors need to be considered in order to obtain a specific polyurethane system, including chemical (OH number, water content, molecular weight) as well as mechanical factors i.e. viscosity of components and final system [5]. The viscosity of the components affects the flow properties of material and therefore the production processes and holding of polyurethane. But the polymer viscosity according to rate at which it is sheared, provides important information with regard to the processing and performance of material, where stirring, dispensing and pumping and the product will be subject it to a variety of shear rates. Low shear behavior can be related to storage conditions of materials, i.e. sedimentation, phase separation and structure retention [19][20]. The knowledge about this issue, rheology, can be useful in the planning of polymer processing where temperature and pressure programs are applied. It gives an insight on the properties of matter that determine its behavior when a mechanical force is exerted on it and partially on the structure by means of the size, shape and distribution of molecules [20][21]. In polyurethane system, the main ingredient is oligomer or polyol (even up to 60-70%) and mostly it is of petrochemical origin [22], hence in order to reduce the percentage of petrochemicals many researchers are focused on introducing renewable substances[23][24] or components from recycling [25][26] into polyurethane formulation. Thus utilizing recycled polyols in polyurethane system is a good way for saving substances from natural resources and at the same time reducing the amount of waste. The price can be an additional advantage, as semi-products from recycling can be cheaper than commercial polyols [5].

To describe the rheology of fluid, mathematical models based on rheograms are proposed [20][27][28]. Besides the Newtonian fluid, three models for non-Newtonian fluids are usually applied. Newtonian fluids are considered to be ideal fluids, performing linearly in rheograms. Newtonian fluids can be described by the following equation:

$$\tau = \eta\dot{\gamma} \,, \qquad (1)$$

where η is viscosity.

In the case of Newtonian behavior, the dynamic viscosity maintains a constant value meaning a linear relationship between shear stress (τ) and shear rate ($\dot{\gamma}$) [27].

Models describing non-Newtonian fluids:

- Bingham model describes the flow curve of a material with a yield stress and a constant viscosity at stresses above the yield stress (i.e. a pseudo-Newtonian fluid behavior). The yield stress is the shear stress at shear rate zero and the viscosity is the slope of the curve at stresses above the yield stress.

$$\tau = \tau_0 + \eta\dot{\gamma} \qquad (2)$$

τ_0 = 0=> Newtonian behavior

τ_0 > 0 => Bingham plastic behavior

- Ostwald model also known as the Power Law model, is applied to shear thinning fluids which do not present a yield stress. This model was developed due to the fact, that for a lot of plastics in a broad range of shear rate, there is a linear dependency between viscosity and shear rate. The *n*-value in equation gives fluid behavior information according to:

$$\tau = K\dot{\gamma}^{n} \tag{3}$$

n < 1 => Pseudoplastic behavior

n = 1 => Newtonian behavior

n > 1 => Dilatant behavior

- Herschel Bulkley model is applied on fluids with a non- linear dependence between shear stress and shear rate and yield stress [29], [30][31]

$$\tau = \tau_0 + K\dot{\gamma}^{n} \tag{4}$$

Due to the pro-ecological attitude, oil industry invests a great quantity of money in renewable resources and tries to replace crude oil using i.e. biodiesel. The main product is methyl esters (biodiesel) and glycerin is obtained as a by-product [32], [33][5].

In this work, the focus of our investigation was to study the rheological effect of the use of different catalysts on resulting product from polyurethane decomposition, where decomposition agent was crude glycerin. Such studies will provide specific information about the structure and the rheological properties which are very important to prepare a system for polyurethane synthesis.

EXPERIMENTAL

Material and methods

Glycerolysis

Flexible polyurethane foam waste based on polyether polyol (M_n=3600 g/mol, OH value=45-50 mg KOH/g, acidity value 0.1 mg KOH/g) and polymeric diphenylmethane- 4,4-diisocyanate (pMDI, Borsodchem, Hungary) was reacted in a decomposition reaction with crude glycerin in weight ratio 3:1. Crude glycerin with a purity of 84% (Rafinferia Trzebinia S.A., Poland) was used as a decomposing agent and six different catalyst, in amount of 0.5% in relation to polymer amount, were used. Applied catalysts are given in Table 1. The parameters of the reaction were the same for each reaction, while the catalyst varied. The reaction was carried out in a 2 L stainless steel reactor with a mechanical stirrer and a reflux condenser in the temperature of 225 - 230°C [34]. In order to compare the obtained semi-products, the reaction was carried out for 30 min for each decomposition. The used catalysts can be divided into two groups due to the reaction and resulting semi-products from glycerolysis: reaction single-phase (catalysts: TEA, KAc, DABCO), homogenous semi-product (GL-TEA, GL-KAc, GL-DABCO) and split-phase reaction (catalysts: NaOH, DbDl, StOc), divided into two phase (liquid and solid) semi product (GL-NaOH, GL-DbDl, GL-StOc). In the split-phase products the ratio between liquid and solid phase was approx. 3:2. Samples after the glycerolysis process were collected from the reactor in a temperature of ca. 80ºC (still liquid form) and poured to glass storage bottles. After cooling down from split-phase samples, the upper phase was decanted to another storage bottle.

Characterization of obtained semi-products

Spectroscopic analysis of glycerolysates was carried out by means of a FTIR Nicolet 8700 spectrophotometer (Thermo Electron Corporation) and the ATR technique. The Specac Heated Golden Gate single reflection diamond ATR accessory was used and it operated up to 200 ºC. Spectra were registered at room temperature for wavenumbers ranging from 500 to 4500 cm^{-1}at 4 cm^{-1} nominal resolution with 64 scans.

^1H NMR spectra of glycerolysates were recorded with a Bruker AV 400MHz spectrometer in $CDCl_3$ solvent at ambient temperature. The simulation and iteration of spectra were carried out using Bruker software.

Hydroxyl value of the recovered polyol was determined by a standard titration method (PN-EN ISO 2554:2001). Each experimental analysis was repeated at least twice and the average value has been given. All chemicals used in this analyze were of the quality required in the standards.

Rheological measurements were performed using a rotary rheometer R/S-CPS+ (Brookfield, USA). Measurement system cone/plate has been applied for rheological testing. The rheological parameters were calculated using the Rheo3000 program. Measurements were conducted with controlled shear rate (CSR). The following program was applied: increasing shear rate from 1 s^{-1} to a certain value for 180 s; constant shear rate for 180 s; and decreasing shear rate from certain to 1 s^{-1} for 180 s. The applied value of shear rate is in correspondence to shear rate ranges in some industrial processes e.g. mixing 10–500 s^{-1}or pumping 10–300 s^{-1} [35]. Based on the rheological measurements, the viscosity and flow curves of glycerolysates at different temperatures were plotted. The rheological models and parameters were defined using the Rheo3000 program.

RESULTS AND DISSCUIONS

Spectroscopy analysis by FTIR and ^{1}H NMR

The chemical structure of obtained glycerolysates was confirmed and compared with original polyol (Polyol) by FTIR spectroscopy (Fig. 1). Generally, the spectra are similar, but some differences can be identified. A very flat peak in the rage 3600 to 3200 cm^{-1} can be observed in the FTIR spectra for glycerolysates indicating the remaining glycerin in the media. The characteristic stretching vibrations of -NH bond, coming from urethane bond occur at 3363 cm^{-1} for all glycerolysates. Intensive absorption bands at wavenumber 2950 - 2870 cm^{-1} correspond to symmetric bending oscillation of $–CH_2$ and $–CH_3$ groups and refer to the main chain of glycerolysate (as well as in original polyol). The magnification of the wavenumber region from 2000 to 700 cm^{-1} is shown in Fig.2 in order to present the main differences between the glycerolysates. The peak at wavenumber 1722 cm^{-1}, characteristic for carbonyl group C=O, occurs for semi-products from single-phase reaction with higher intensity [36]. This peak can correspond to transesterification products, carbamates (glycerolysis by-product) and urethane groups of the original foam [26]. Hereby, it can be concluded, that in the split-phase obtained glycerolysates, the by-products are in a minor quantity. The schematic process of forming carbamates during glycerolysis is shown in Schemes 2 – 3 [5]. The absorption bands at 1610 and 1590 cm^{-1} correspond to bending vibrations of –NH and indicate that glycerolysates contain carbamates and amines as a derivate from breaking of urethane bonds. The region of ca. 1530 cm^{-1} corresponds to the stretching vibrations of –NH in primary amines. Hence, absorption bands at 1610, 1590 and 1530cm^{-1} are related to the bending vibrations of amine groups derived from pMDI, which has been dissolved within the products. However, FTIR spectra corresponding to glycerolysates obtained in split-phase reaction present those band with lower intensity. Bands visible at 1520-1350 cm^{-1} are attributed to deformational oscillation of $–CH_3$ groups and other oscillation from the bonds between carbon atoms. The absorption bands in the spectral region in 1465 and 1388 cm^{-1} are associated with characteristic bending vibrations of methylene and methyl groups in the polyol chain [37]. The C–O (urethane) band of urethane bonds at 1220 cm^{-1} appears only for glycerolysates obtained from single-phase and it can be assumed that those samples are more contaminated with carbamates. The C–O band at 1008 cm^{-1} derived from hydroxyl compounds present in glycerolysates is assigned to C-O in the polyol chain, attributed to the stretching vibrations of C-O-C bond [23]. This bending vibrations are characteristic for ether group in ether polyol.

Fig. 3 presents ^{1}H NMR spectra of two selected glycerolysates, from split-phase (GL-NaOH) and single-phase (GL-KAc) in comparison with spectra of original polyol and pMDI used in polyurethane foam synthesis. The structures of the original components are shown in Fig. 3 and the main protons in these compounds are marked by letters and assigned to peaks in the spectra. In general, the spectra of glycerolysates are quite similar to polyol spectrum, with the main peaks at the same chemical shifts. However, some additional peaks, which can be found in pMDI spectrum are visible (peaks connected with aromatic rings but with much lower intensity), hence indicating some contamination of glycerolysate with an isocyanate derivate.

Peak at 1.15 ppm corresponds to methyl equivalent hydrogen's ($-CH_3$) and represents a side chain the polyol and as well in glycerolysates. The multiple peaks visible in the range of 3.4 to 4.0 ppm are related to methylene hydrogen's ($-CH_2-$) and hydrogen's that their carbons are directly connected to the oxygen ($-CH_2-O-$) [38]. In the region of 6.7 to 7.1 ppm in spectra of glycerolysates, there are peaks associated with hydrogen's in aromatic rings derived from pMDI, therefore indicating some contamination of these compounds. However, for the GL-KAc sample these peaks are with higher intensity than for GL-NaOH. Additionally, peaks characteristic for hydrogen's in aromatic rings for GL-StOc are shifted to lower values, probably derived from aromatic amines. Similar situation was observed by Nikje et al.[37].

Hydroxyl value

Hydroxyl values are presented in Table 2. The main observation is that depending on the direction of reaction (catalyst), the hydroxyl number differs for glycerolysates obtained through singe-phase and split-phase. For single-phase and split-phase glycerolysate the values of OH_{number} are greater than 250 and 100 mg KOH/g, respectively. This feature can be a result of the remaining glycerin in the single-phase glycerolysates. However, for split-phase glycerolysates the excess of glycerin stayed in the bottom phase, as well with other by-products, therefore the hydroxyl number is lower for those glycerolysates. The obtained semi-products with hydroxyl values in the range of approx. 150-300 mg KOH/g could be used as a polyol for viscoelastic foam formulations, in which very often a set of several different types of polyols with different chain lengths and different hydroxyl number are used [39].

Rheology

The following program was applied: increasing shear rate from 1 to 100 s^{-1} for 180 s; constant shear rate of 100 s^{-1} for 180 s; and decreasing shear rate from 100 to 1 s^{-1} for 180 s to obtain the flow and viscosity curves and the rheological model.

Flow curves

The Figs. 4(a,b,c) and 5(a,b,c) show the rheograms of ,obtained in split-phase reaction, glycerolysates at 25, 50 and 60 ^{o}C and in single-phase reaction at 60, 70 and 80 ^{o}C, respectively. Different temperatures were chosen due to different physical form of glycerolysates (glycerolysates obtained in split-phase reaction were liquid like, but obtained in single-phase reaction were more viscous) and their ability to flow at determined temperatures and shear rate. In Fig. 4 the flow curves of split-phase glycerolysates are presented and a large reduce of shear stress (ca. five times) with rising temperature from 25 to 50 ^{o}C can be noticed. A subsequent temperature increase of about 10 ^{o}C causes a two times lower shear stress. With increasing temperature, the shear stress is decreasing. With higher temperature, the flow curves are not so linear as at the beginning and the small hysteresis loops are formed, consequently these samples tend to be rheopectic fluids, where viscosity increases under an imposed shearing action [40]. The occurrence of hysteresis can be explained by the existence of different molecules, with short and long chains and the longer chains start to move with higher temperature. The values of shear stress at 60 ^{o}C for samples obtained in split-phase glycerolysis are approx. 21 Pa, but for semi-products obtained in single-phase glycerolysis are in the range ca. 500-1000 Pa. Such a big difference results from the entirely different appearance of samples, as it was mentioned before. It can be estimated that shear stress values, as well as the reaction, depend on the kind of catalyst in applied conditions. From split-phase glycerolysis only the upper phase is tested and considered as the valuable one, similar to polyol. The bottom phase consists of the amines, the rest of unreacted glycerin, so almost 40% of the product will have limited number of use cases in some industrial applications [41] [15]. The samples form split-phase show very similar shear stress, so it can be concluded that the obtained products are similar and the choice of catalyst can be up to other properties. The lowest shear stress in all temperatures from single-phase products indicates sample obtained with potassium acetate used as catalyst. Also in the case of these glycerolysates with higher temperatures the narrow hysteresis loops are formed. Forming of hysteresis loops is related with exhibiting thixotropy in the materials, whereas fluid's viscosity decreases over time under an imposed constant shear rate [35].

Rheological model Hershel Bulkley

In Table 3, the parameters from Herschel Bulkely model are presented. The results were calculated and obtained from the Rheo3000 program. Herschel-Bulkley was chosen as an optimal model to describe flow curves (Fig. 6) due to the highest determination coefficient (R^2). This model is described by the following equation:

$$\tau = \tau_0 + m \cdot \dot{\gamma}^n \tag{4}$$

where τ is shear stress (Pa), τ_0 is yield stress (Pa), m is the consistency index (Pa·s), n is the flow index and $\dot{\gamma}$ *is the* shear rate (s^{-1}).

The results show that the glycerolysates exhibit different types of fluid behavior and can be described as non-Newtonian and Newtonian fluids. The difference could be seen in the presented flow curves in Figs. 4-5. For fluids described by Herschel Bulkely model, we can divide the materials into different types of fluid using, among others, the flow index from database (*n*). When the flow behavior index is close to 1 the fluid's behavior tends to pass from a shear thinning to a shear thickening fluid. When *n* is above 1, the fluid acts as a shear thickening fluid, below as a shear thinning fluid. The equations below give fluid behavior information as follows:

$\tau_0 = 0$ & $n = 1$ → Newtonian behavior

$\tau_0 > 0$ & $n = 1$ → Bingham plastic behavior

$\tau_0 = 0$ & $n < 1$ → Pseudoplastic behavior

$\tau_0 = 0$ & $n > 1$ → Dilatant behavior [42]

Therefore, the usage of different catalyst can result in obtaining different semi-products, which will result in the need of different parameters during processing. Re-polyols obtained in split-phase process in applied conditions (shear rate 0-100 s^{-1}, temperatures 25-60 ^oC) have the flow index higher than 1, so they are dilatant fluids and their behavior is shear thickening. Dilatant fluids become thicker when agitated, i.e. the viscosity increases proportionally with the increase of the shear rate. When stress is removed, a dilatant system returns to its original state of fluidity. The flow index of GL-TAm is approx. 1 for all temperatures, so it means that in applied conditions this material is considered as Newtonian fluid. For Newtonian fluids the dynamic viscosity maintains a constant value, signifying a linear relationship between the shear rate and shear stress, that conjuncture can be observed in Fig.5. Newton assumed that all materials have, at a given temperature, a viscosity that is independent of the shear rate. In other words, twice the force would move the fluid twice as fast [29]. The GL-KAc sample indicated Newtonian behavior up to 70 ^oC, at 80 ^oC the sample indicated pseudoplastic behavior. The GL-DABCO sample has a flow index below 1, and its behavior is pseudoplastic in all temperatures (shear thinning). Pseudoplastic fluids become thinner when the shear rate increases, until the viscosity reaches a plateau of limit viscosity. This behavior is caused by increasing the shear rate and the elements suspended in the fluid will follow the direction of the current. There will be a deformation of fluid structures involving the breaking of aggregates at a certain shear rate and this will cause a limit in viscosity. For pseudoplastic fluids the viscosity is not affected by the amount of time the shear stress is applied as these fluids are non-memory materials i.e. once the force is applied and the structure is affected, the material will not recover its previous structure. As the shearing stress is increased, disarranged molecules orient themselves to the direction of the flow. This orientation reduces internal friction and resistance of the molecules and allows a greater rate of shear at each shear stress [40], [42].

The consistency index (*m*) gives an idea about the viscosity of the fluid, the higher it is, the higher the viscosity exhibited by the material.

Viscosity curves

In Figs. 7-8 the viscosity curves are presented. The testing parameters were the same as for the flow curves. The viscosity arises from the interaction among the particles in substance. It can be notice that the curves indicate such character as it is described by mathematical models. So the model chosen to describe this behavior, Herschel-Bulkley, is a good one. Also, as we can see in Table 3, with higher temperature, the consistency index (*m*) decreases, as does viscosity. The re-polyols obtained from split-phase glycerolysis (Fig. 7) exhibit shear thickening in all temperatures where with higher shear rate, the viscosity is increasing [22]. The glycerolysates obtained in single phase reaction, the viscosity curves (Fig. 8) are represented by an almost straight line. Viscosity is independent of the shear stress or shear rate; that is, the polyols displayed Newtonian behavior. Sample GL-DABCO indicates a shear thinning behavior in all temperatures, but it is poorly visible, as the flow index is close to 1. The observed shear thinning behavior can be explained by changes in the orientation of molecules caused by the flow field. The molecules passing in the flow field change their direction by rotation, to become parallel to the flow direction. This configuration results in lower frictional resistance as well as lower viscosity [19]. Decreasing shear rate and viscosity with increasing temperature is connected to the increased movement of macromolecules and the free volume between them [43].

Behavior type depending on different parameters

In order to verify the changes in rheological behavior of obtained semi-products, the rheological measurements with different parameters were performed. The applied conditions and the program described in *Characterizations of obtained semi-products* of measurements are shown in Tables 4 and 5.

In Fig. 9a, the results of dependence of different shear rates from 100 to 300 s^{-1} on the flow index, for samples at 60 and 80 ^{o}C for semi-products of split- and single-phase are shown, respectively. The samples obtained in split-phase reaction indicate lowering of flow index with higher shear rate, similar trend occurs for single-phase product, expect for the GL-KAc sample, which shows the opposite trend. This conjuncture is due to the fact that for GL-KAc in higher shear rate, the Ostwald model is more suitable (determination coefficient is closer to 1).

Fig. 9b shows the relationship between the flow index and the temperature. As we could notice in Table 3, with rising temperature, the flow index is increasing, especially for split-phase re-polyols. With the higher temperature, those materials become more thickened. Like in the case described above, the GL-KAc differs from others and for those samples the index flow decreases with higher temperature.

CONCLUSIONS

Re-polyols, obtained from polyurethane foam chemical recycling via crude glycerin, are valuable semi-products and can be applied in polyurethane synthesis e.g. partially replacing commercial polyol. Such action not only allows to reduce amount of polyurethane waste, but will also help to reduce the usage of petrochemical substances. Usage of different catalysts in polyurethane decomposition resulted in obtaining different semi-products with different physical appearance and rheological behavior, in applied condition. However, the chemical structure confirmed by FTIR was not influenced significantly by the type of catalyst. But yet, in FTIR spectra of split-phase glycerolysates the C=O peak from carbamates and peaks associated with N-H were much less intensive in comparison with single-phase glycerolysates, therefore it can be said that those samples were not much contaminated. That was also confirmed using ^{1}H NMR spectroscopy, where peaks at chemical shifts associated with isocyanate derivate were with higher intensity for single-phase glycerolysate. The hydroxyl values were in the range of 150-300 mg KOH/g, typical for viscoelastic polyols. Rheological measurements can help to prepare the appropriate conditions of processing polyol and polyurethane systems in production. Acquiring the knowledge about the rheology of recycled polyol is connected to its further application in polyurethane synthesis e.g. mixing systems. Therefore, it is considered that there are many factors such as molecular architecture, molecular weight, chemical composition, which affect the rheology. Moreover, the viscosity of a formulation is related to the dynamic extension and segment density, which depends on the volume of a molecule and intermolecular chain entanglement [43]. The information of glycerolysates rheology can be used in mathematical simulations which are necessary for modeling the processing of polyurethane systems with different chemical properties and chemical structure. From the obtained results we can easily attribute specific parameters for mixing glycerolysates. The broad analysis about used catalyst allows to choose the most appropriate catalyst to planed experiments. If it is desired to carry out the process in the split-phase way, the sodium hydroxide can be a cheap and effective catalyst for this process, but if we want obtain homogenous product with quite low viscosity, potassium acetate can be an appropriate catalyst.

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FIGURES CAPTIONS

FIG. 1. FTIR spectra of resulting semi-products, obtained with different catalyst.

FIG. 2. The differences between FTIR spectra of glycerolysates.

FIG. 3. ^{1}H NMR spectra of glycerolysates GL-NaOH, GL-KAc, origin polyol and pMDI.

FIG. 4. Flow curves of samples obtained in split-phase glycerolysis at 25 (a), 50 (b) and 60 ^{o}C (c).

FIG. 5. Flow curves of samples obtained in single-phase glycerolysis at 60 (a), 70 (b) and 80 ^{o}C (c).

FIG. 6. Flow curves with trend lines of glycerolysates at 60 ^{o}C for GL-TEA, GL-DABCO, GL-KAc and at 25 ^{o}C for GL-NaOH, GL-DbDl, GL-StOc.

FIG. 7. Viscosity curves of samples obtained in split-phase glycerolysis at 25 (a), 50 (b) and 60 ^{o}C (c).

FIG. 8. Viscosity curves of samples obtained in single-phase glycerolysis at 60 (a), 70 (b) and 80 ^{o}C (c).

FIG. 9. Dependence of the flow index of shear rate (a) and temperature (b) (at shear rate 100 s^{-1}) .

SCH. 1. Proposed mechanism for PU decomposition catalyzed by KOH. [Adapted by [11]].

SCH. 2. Schematic reaction of forming monocarbamates during polyurethane glycerolysis.

SCH. 3. Schematic reaction of forming dicarbamates during polyurethane glycerolysis.

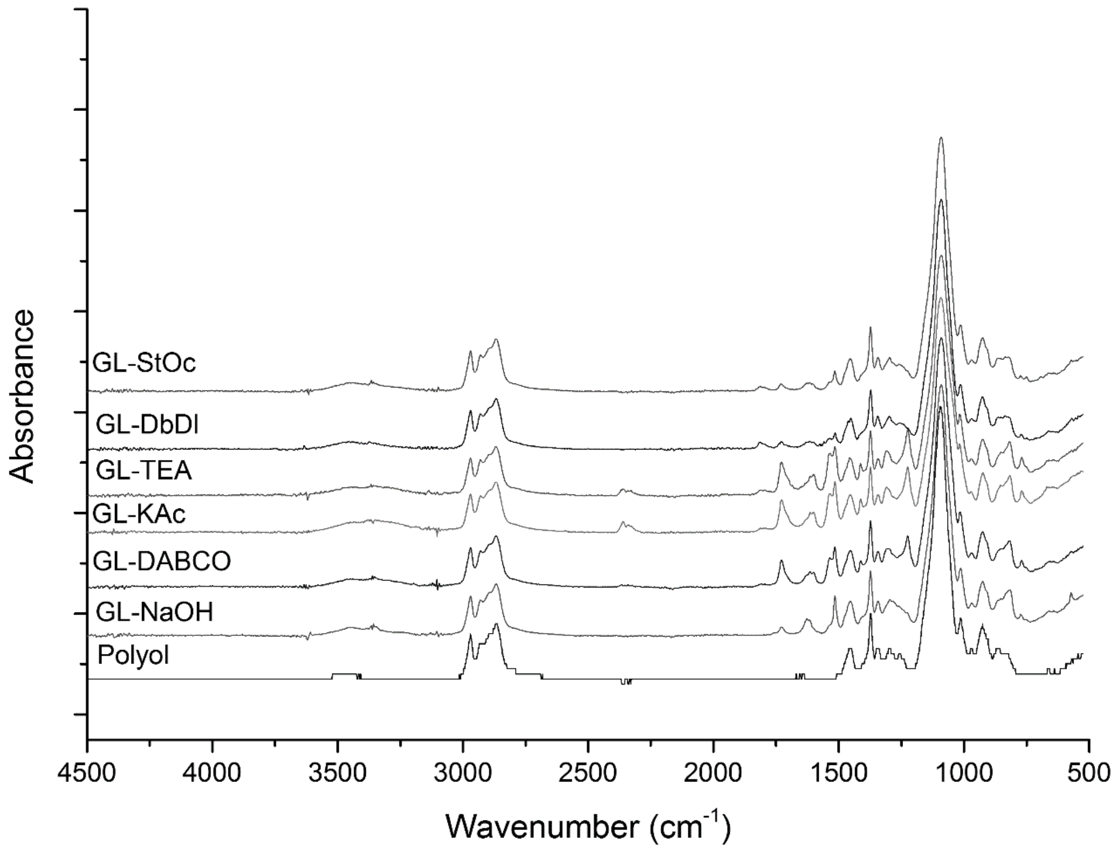


FIG. 4. FTIR spectra of resulting semi-products, obtained with different catalyst.

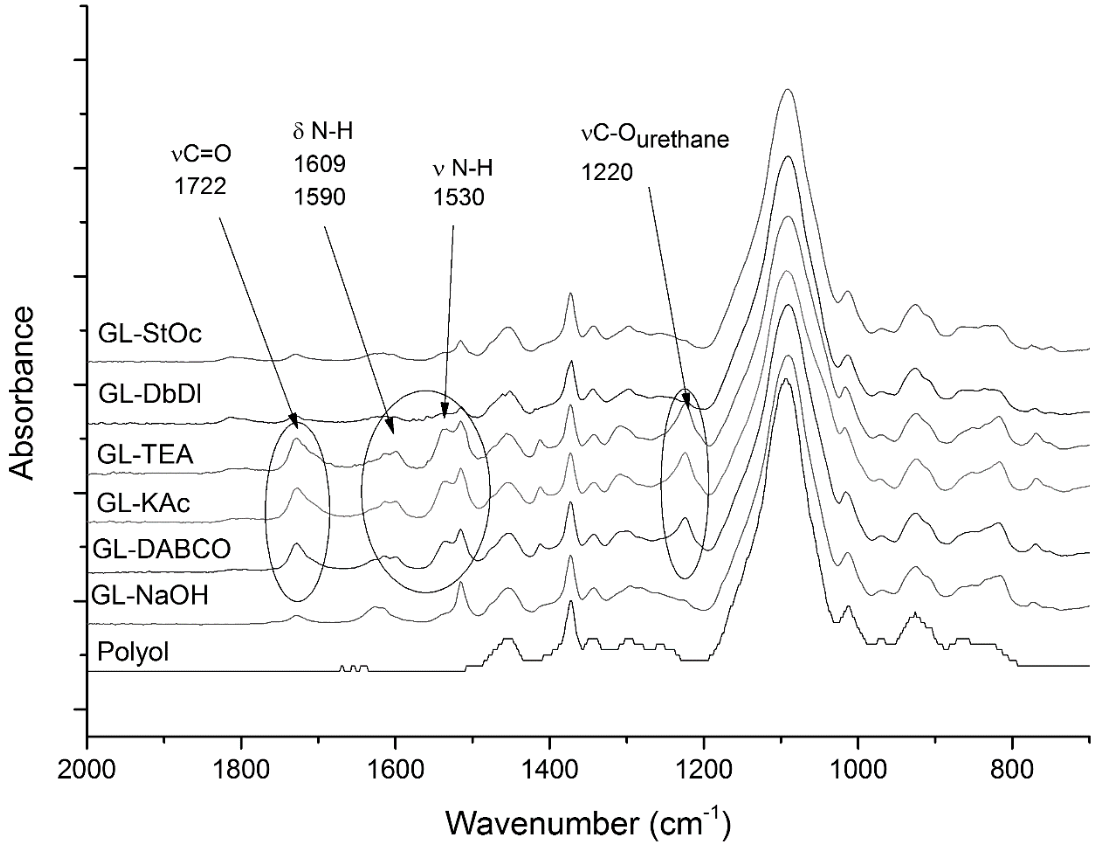


FIG. 5. The differences between FTIR spectra of glycerolysates.

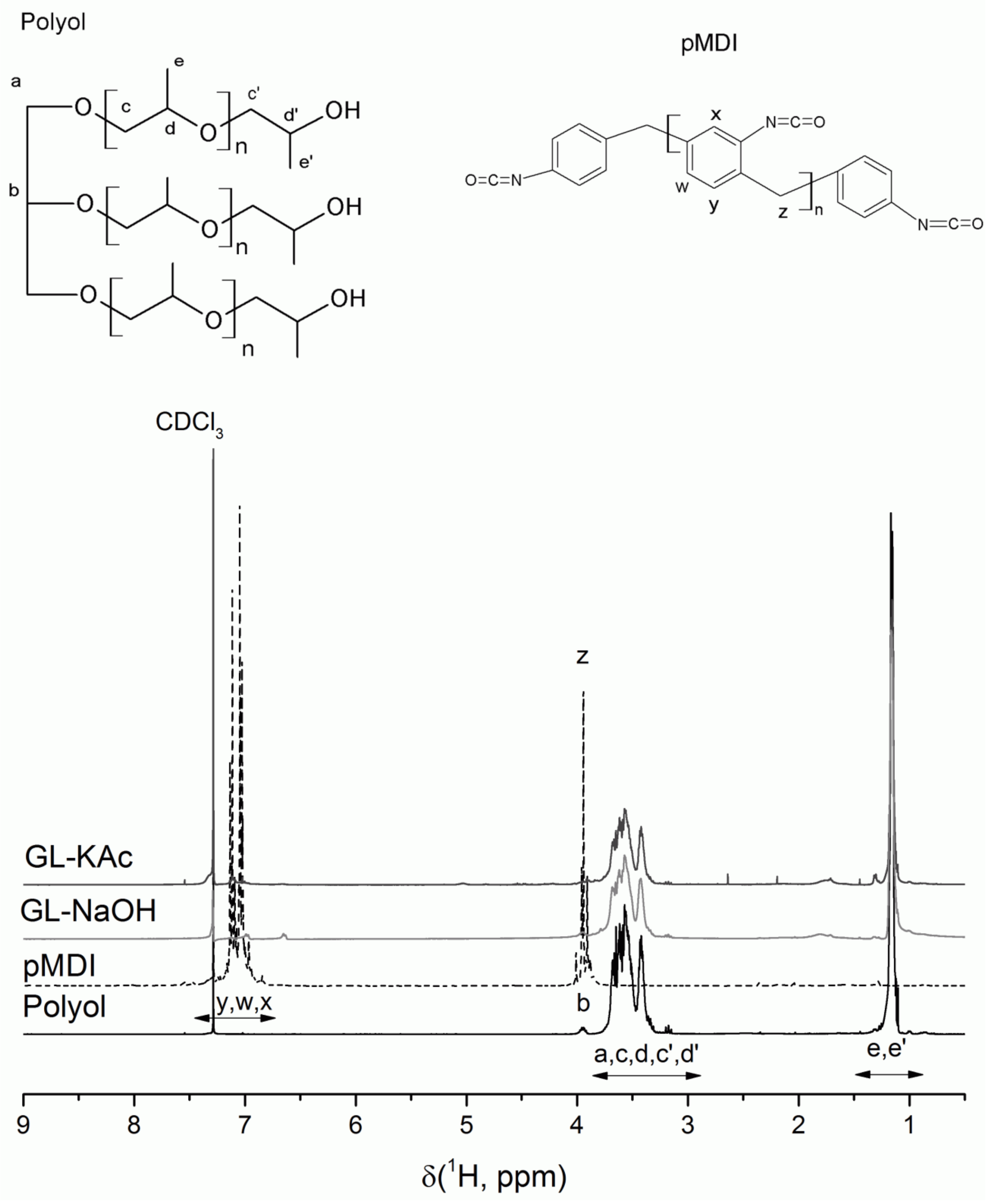


FIG. 6. ^{1}H NMR spectra of glycerolysates GL-NaOH, GL-KAc, origin polyol and pMDI.

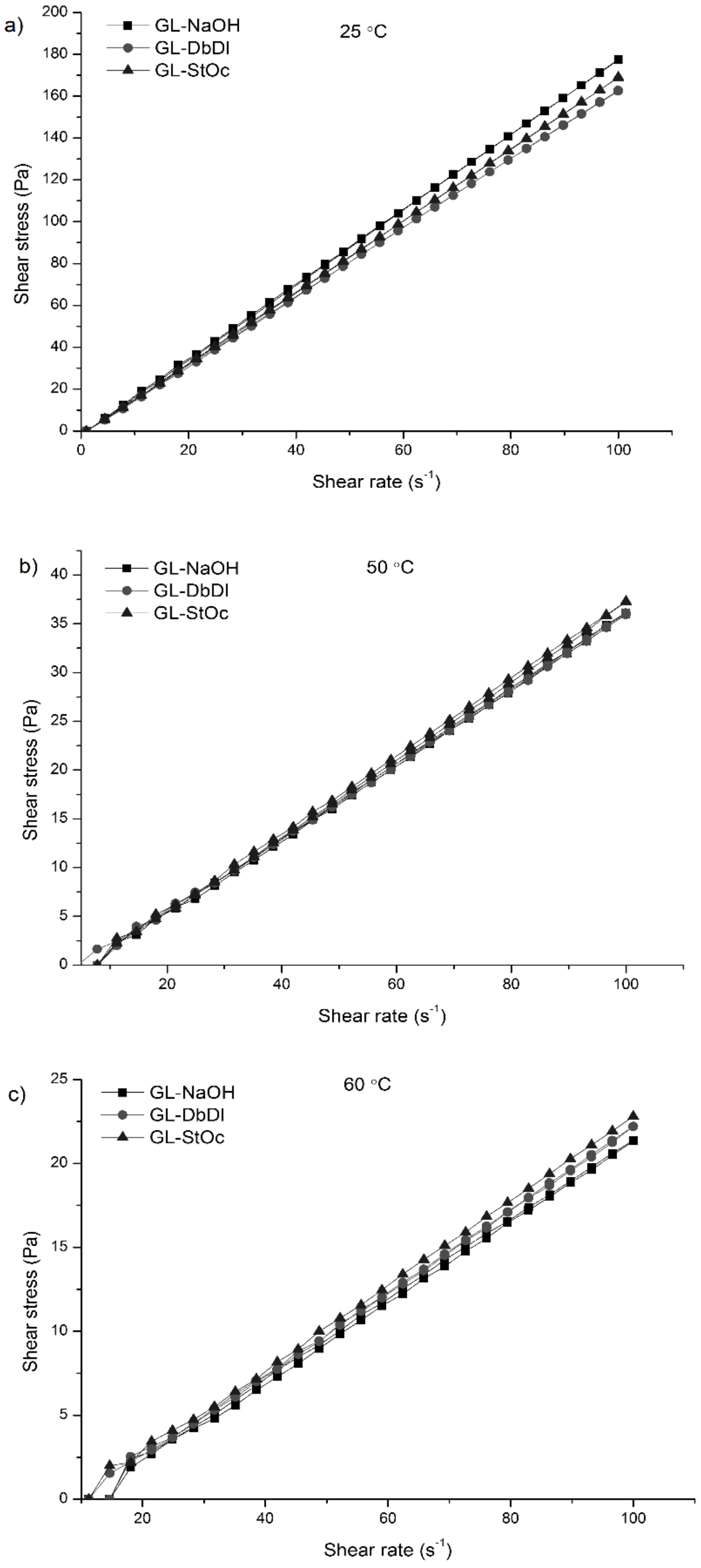


FIG. 4. Flow curves of samples obtained in split-phase glycerolysis at 25 (a), 50 (b) and 60 ^{o}C (c).

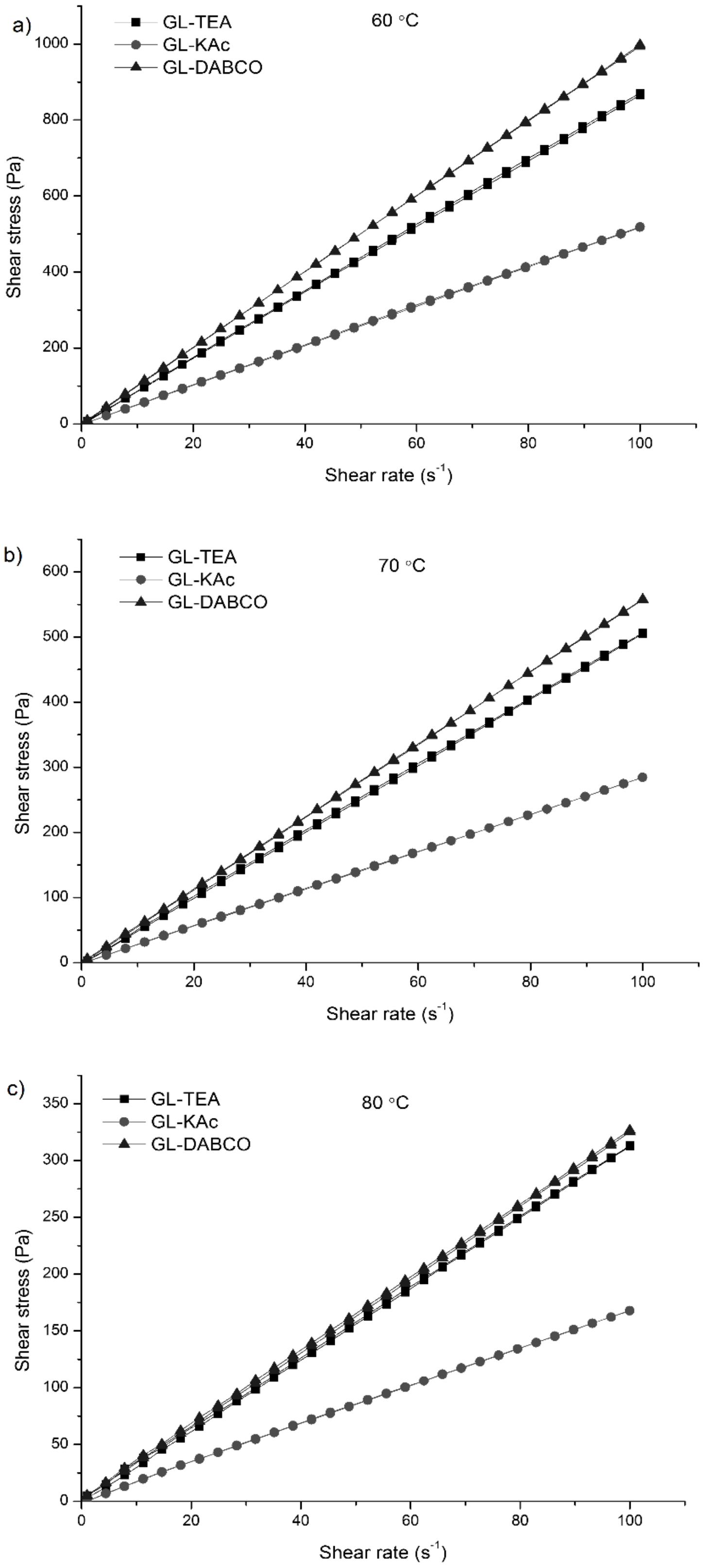


FIG. 5. Flow curves of samples obtained in single-phase glycerolysis at 60 (a), 70 (b) and 80 °C (c).

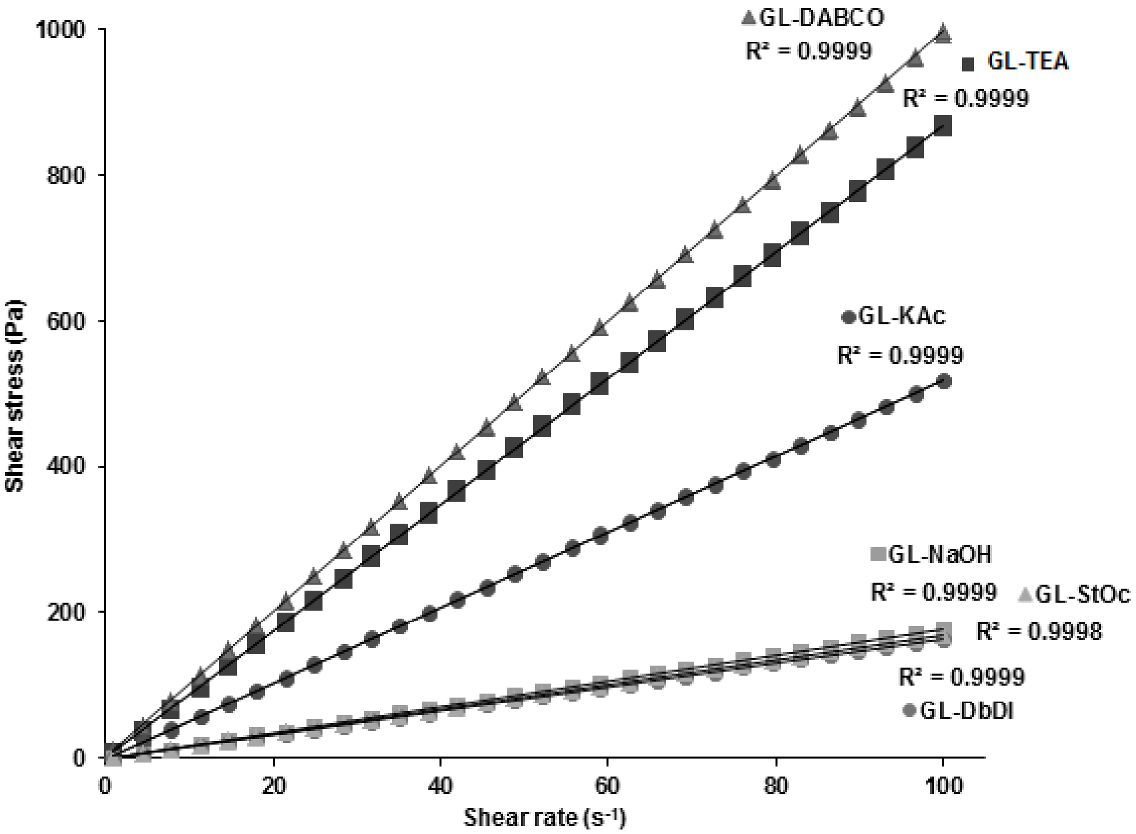


FIG. 6. Flow curves with trend lines of glycerolysates at 60 ºC for GL-TEA, GL-DABCO, GL-KAc and at 25 ºC for GL-NaOH, GL-DbDl, GL-StOc.

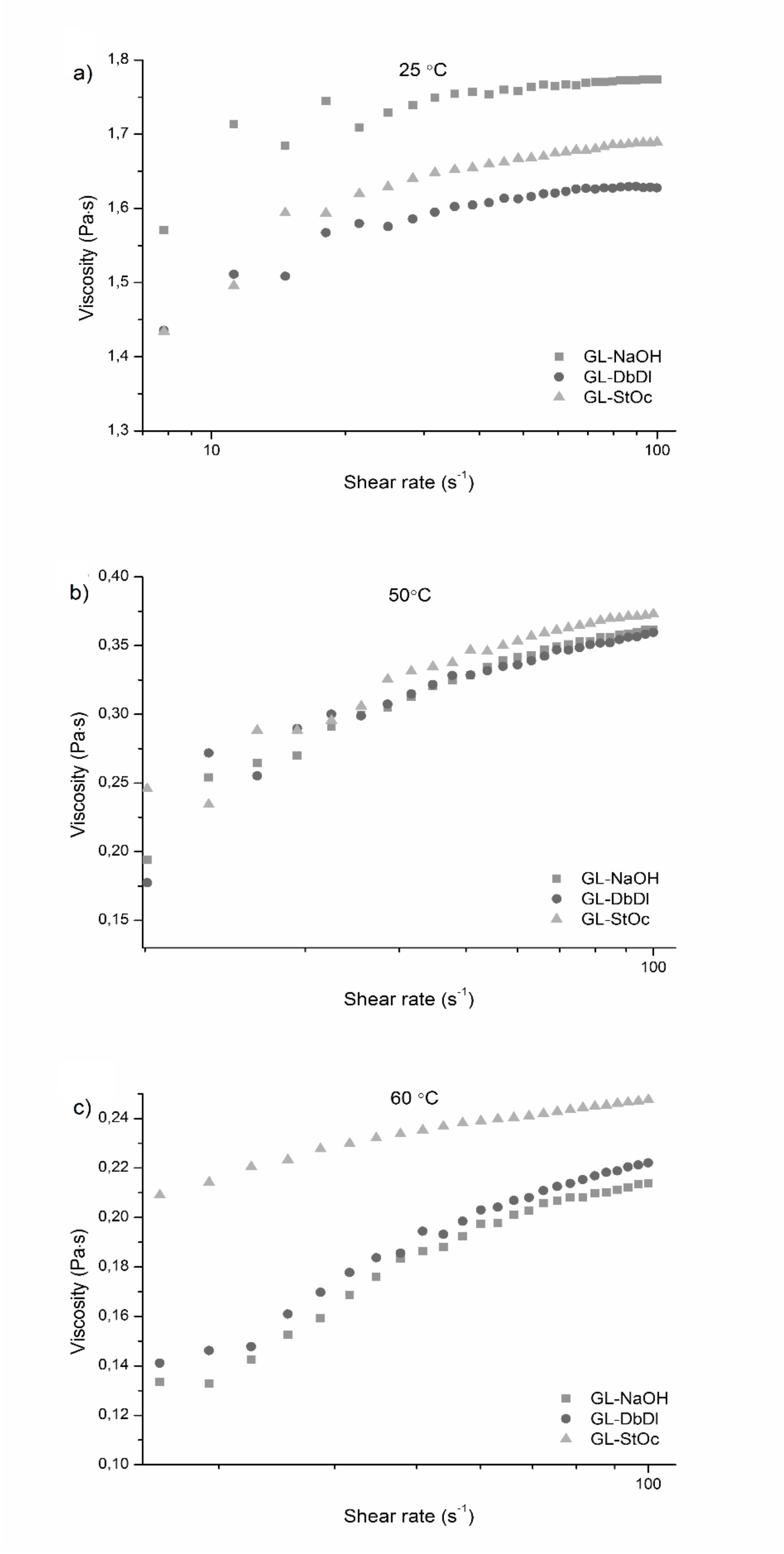


FIG. 7. Viscosity curves of samples obtained in split-phase glycerolysis at 25 (a), 50 (b) and 60 °C (c).

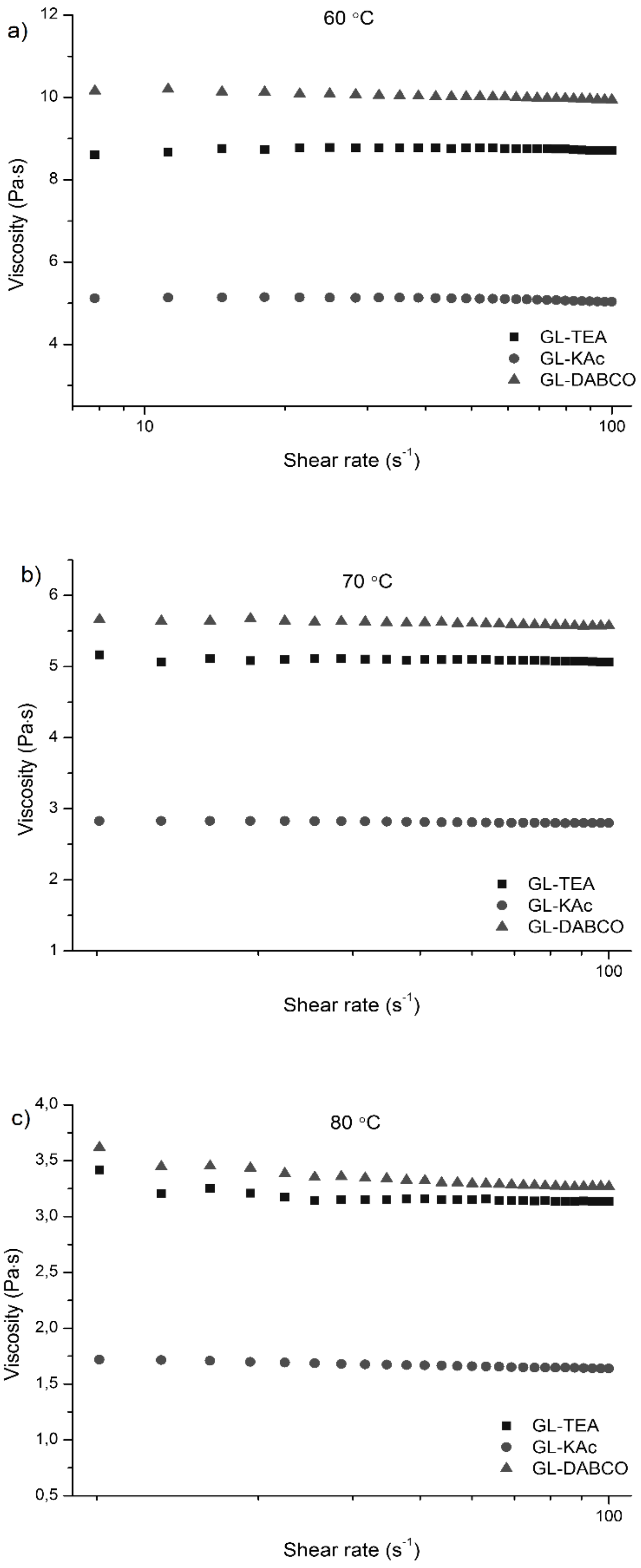
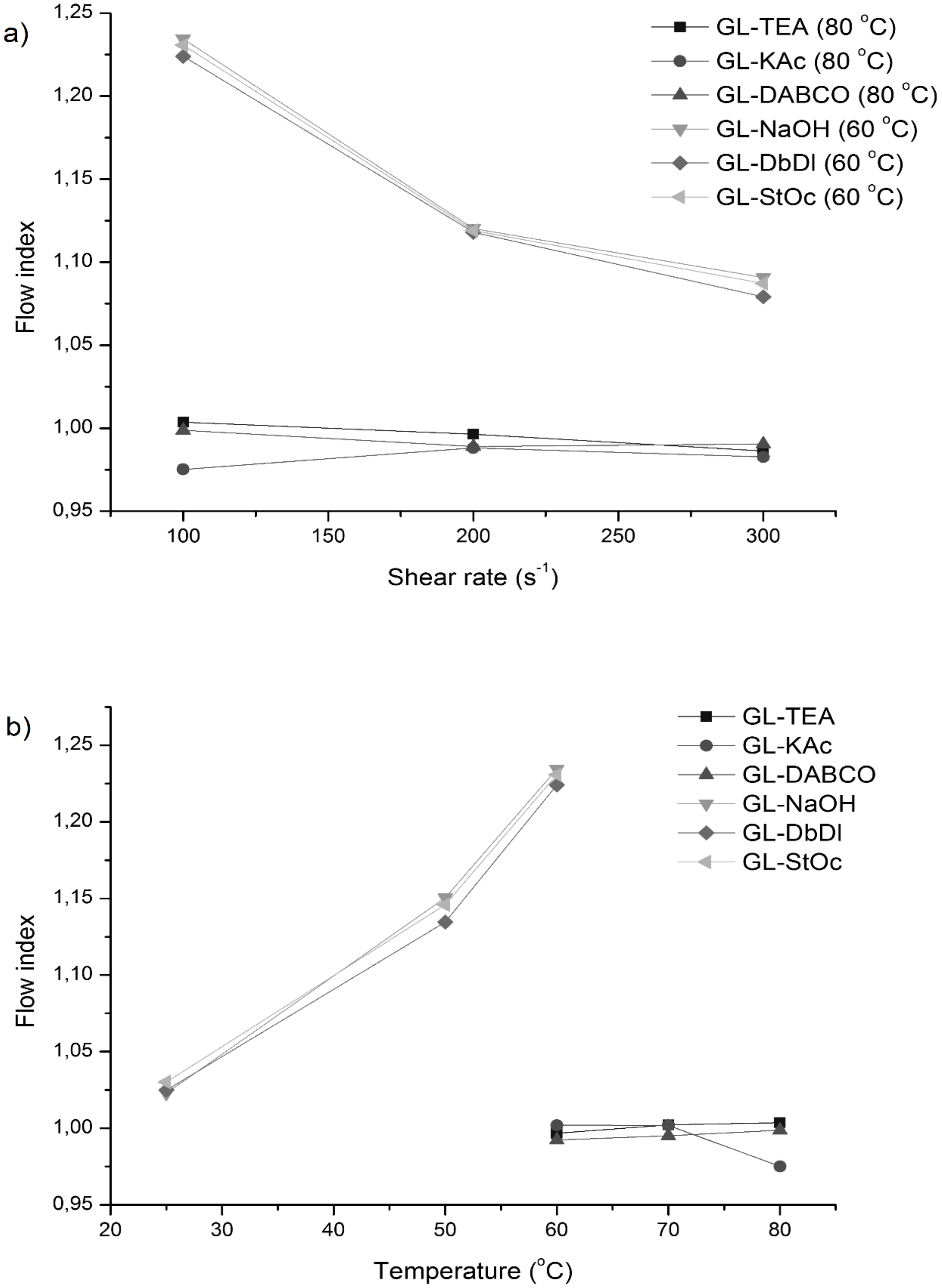


FIG. 8. Viscosity curves of samples obtained in single-phase glycerolysis at 60 (a), 70 (b) and 80 ^{o}C (c).



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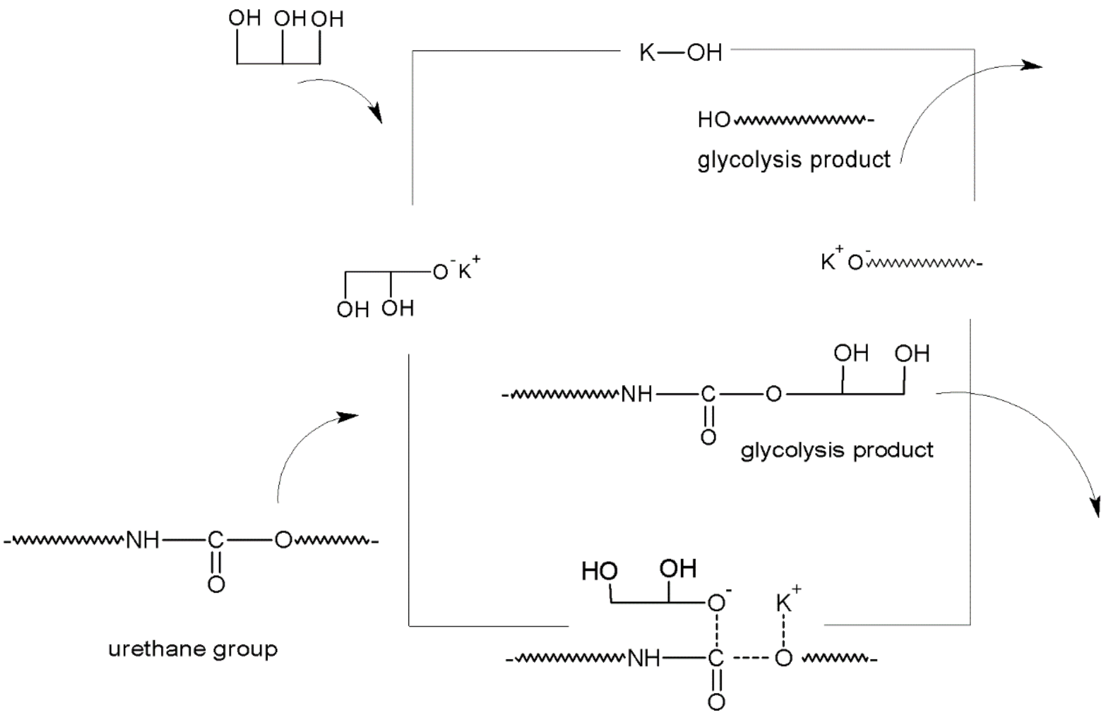

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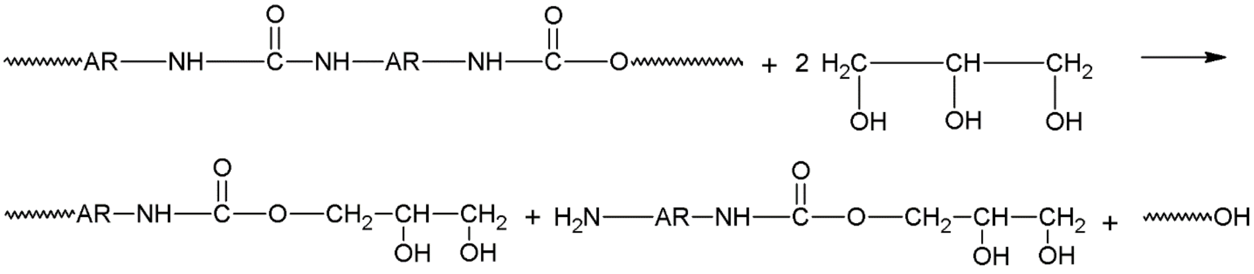
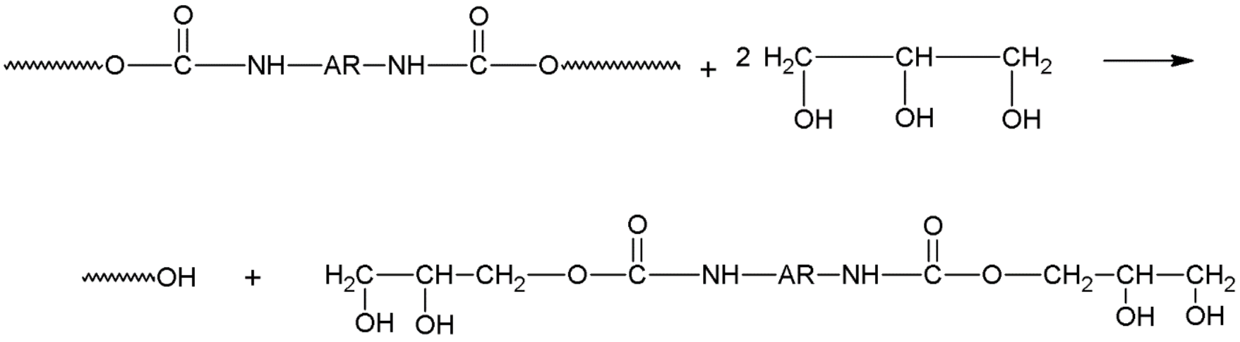


SCH. 4. Schematic reaction of forming monocarbamates during polyurethane glycerolysis.



SCH. 3. Schematic reaction of forming dicarbamates during polyurethane glycerolysis.

TABLES CAPTIONS

TABLE 1. Used catalysts and re-polyols codes with various catalysts.

TABLE 2. Determined hydroxyl number values obtained glycerolysates.

TABLE 3. The Herschel Bulkley linear functions based on the rheological data glycerolysates samples.

TABLE 4. Applied parameters for semi-products obtained in split-phase reaction.

TABLE 5. Applied parameters for semi-products obtained in single-phase reaction.

TABLE 2. Used catalysts and re-polyols codes with various catalysts.

Catalyst	Producer	Code of glycerolysate	Type of reaction	Approx. Price
Triethylamine (TEA)	Sigma Aldrich, Poland	GL-TEA	Single-phase	123€/1 l
Potassium acetate (CH_3COOK, KAc)	POCH, Poland	GL-KAc	Single-phase	44€/1 kg
1.4-diazabicyclo[2.2.2]octane (DABCO)	Sigma Aldrich, Poland	GL-DABCO	Single-phase	250 €/1 kg
Sodium hydroxide (NaOH)	POCH, Poland	GL-NaOH	Split-phase	12€/1 kg
Dibutylin dilaurate (DbDl)	Merck Millipore, Poland	GL-DbDl	Split-phase	95€/1 l
Tin (II) 2-ethylhexanoate Stannous octoate (StOc)	Sigma Aldrich, Poland	GL-StOc	Split-phase	210 €/1 kg

TABLE 2. Determined hydroxyl number values obtained glycerolysates.

Sample	**GL-TEA**	**GL-KAc**	**GL-DABCO**	**GL-NaOH**	**GL-DbDl**	**GL-StOc**
I_{OH} (mg KOH/g)	261	284	255	140	144	131

TABLE 3. The Herschel Bulkley linear functions based on the rheological data glycerolysates samples.

Sample	T (°C)	τ_0	m (Pa s^n)	n	Behavior	R^2
GL-NaOH	25	-	1.5995	1.0228	Shear thickening	0.9999
	50	-	0.1823	1.1505	Shear thickening	0.9990
	60	-	0.0738	1.2344	Shear thickening	0.9976
Gl-DbDl	25	-	1.4567	1.0248	Shear thickening	0.9998
	50	-	0.1952	1.1346	Shear thickening	0.9993
	60	-	0.0802	1.224	Shear thickening	0.9984
Gl-StOc	25	-	1.4725	1.0302	Shear thickening	0.9999
	50	-	0.1921	1.1459	Shear thickening	0.9988
	60	-	0.0799	1.2307	Shear thickening	0.9981
GL-TEA	60	-	8.8088	0.9967	Shear thinning	0.9999
	70	-	5.0057	1.0023	Newtonian	0.9998
	80	0.8839	3.0666	1.0037	Newtonian-Bingham plastic	0.9998
GL-KAc	60	-	5.1319	1.002	Newtonian	0.9999
	70	-	2.8206	1.0019	Newtonian	0.9999
	80	-	1.8821	0.9752	Shear thinning	0.9999
GL-DABO	60	-	10.2966	0.9924	Shear thinning	0.9999
	70	-	5.7023	0.9952	Shear thinning	0.9999
	80	2.4861	3.2443	0.9988	Shear thinning	0.9998

TABLE 4. Applied parameters for semi-products obtained in split-phase reaction.

Shear rate	Temperature								
	25 ^{o}C			50 ^{o}C			60 ^{o}C		
100 s^{-1}	GL-NaOH	GL-DbDl	GL-StOc	GL-NaOH	GL-DbDl	GL-StOc	GL-NaOH	GL-DbDl	GL-StOc
200 s^{-1}	GL-NaOH	GL-DbDl	GL-StOc	GL-NaOH	GL-DbDl	GL-StOc	GL-NaOH	GL-DbDl	GL-StOc
300 s^{-1}	GL-NaOH	GL-DbDl	GL-StOc	GL-NaOH	GL-DbDl	GL-StOc	GL-NaOH	GL-DbDl	GL-StOc

TABLE 5. Applied parameters for semi-products obtained in single-phase reaction.

Shear rate	Temperature								
	60 °C			70 °C			80 °C		
100 s^{-1}	GL-TEA	GL-KAc	GL-DABCO	GL-TEA	GL-KAc	GL-DABCO	GL-TEA	GL-KAc	GL-DABCO
200 s^{-1}	-	GL-KAc	-	GL-TEA	GL-KAc	GL-DABCO	GL-TEA	GL-KAc	GL-DABCO
300 s^{-1}	-	GL-KAc	-	GL-TEA	GL-KAc	-	GL-TEA	GL-KAc	GL-DABCO