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Synthesis of Polyurea Thickeners for Perspective Greases

Valeriy Yulyevich Senichev*, Vladimir Nikolayevich Strel'nikov, Vasiliy Vasilyevich Tereshatov, Alexey Igorevich Slobodinyuk, Svetlana Fedorovna Krasnoselskikh

Institute of Technical Chemistry of the Ural Branch of the Russian Academy of Sciences, Perm, Russia

***Corresponding author:** Valeriy Yulyevich Senichev, "Institute of Technical Chemistry of the Ural Branch of the Russian Academy of Sciences" - a branch of the Perm Federal Research Center of the Ural Branch of the Russian Academy of Sciences, Perm, Russia. Tel: +7-3422378274; Email: senichev85@yandex.ru

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Abstract

TTwo methods of the synthesis of polyurea thickeners for greases were proposed, in the VM-6 vacuum oil and in the toluene medium. A number of thickener samples were obtained based on 2,4-toluylene diisocyanate and Isophorone diisocyanate. It was demonstrated that a wider range of polyurea thickeners can be applied using toluene as a dispersion medium for the synthesis. Comparative data on Thermostability of polyurea greases based on two diisocyanates were presented.

Keywords: Diisocyanate; Greases; Polyurea; Thickener

Introduction

Polyurea thickeners are known for their application for greases with improved resistance to work under conditions of elevated temperatures and radiation exposure [1,2]. An important feature of polyurea greases is a control of their molecular structure by hydrogen bonding whereas in the case of soap base greases such control is performed by weaker Van der Waals forces. Such polyurea greases are widely used in automotive and defense engineering, mining and metalworking [3-7].

Some features of polyureas and polyurea thickeners synthesis were described elsewhere; the role of various reaction mechanisms and types of reactants was discussed [8]. It should be noted that aliphatic and aromatic mononuclear diisocyanates are used for polyurea thickeners more often [9-11]. Synthesis of polyurea thickeners based on, as a rule, above mentioned diisocyanates is usually carried out in the environment of oils being the object of thickening, which makes greases manufacturing much easier. However, the process of manufacture of mentioned greases can be complicated for some oils on the synthetic base due to the less colloidal stability of the polyurea gels in other dispersion media [7]. However, polyurea greases can be made using powder thickeners synthesized in hydrocarbon volatile media with its further removal. Therefore, developing synthesis of effective thickeners in volatile media is actual for developing perspective polyurea greases on the base of various synthetic oils. The aim of this work was to study the conditions for the synthesis of polyureas based on Toluene Diisocyanate (TDI) and Isophorone Diisocyanate (IPDI) in toluene medium on the properties of oil-thickener mixtures using aliphatic and aromatic amines.

Materials and Methods

Two diisocyanates were used: 2,4-toluene diisocyanate (99% purity) from Lyondell Basell Netherlands, and Isophorone diisocyanate (isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate) from Bayer, as well as diamines from Alfa Aesar: ethylene diamine and α-octylamine (99% purity). Two oils were used as the hydrocarbon base of greases: distillate oil I-50A, and vacuum oil VM-6. Toluene used as a medium for the polyureas synthesis, was previously dehydrated with freshly calcined molecular sieves (4Å).

Micrographs of the obtained gel samples were obtained on an optical microscope OLIMPUS X501 with a digital photo microscopy system. The completeness of the reaction was determined by the presence of reactive isocyanate groups in the system by FTIR-spectroscopy method using a characteristic absorption band of 2265-2275 cm^{-1} on a Bruker IFS-66/S IR Fourier spectrometer. Samples were prepared according to the procedure described earlier [12]. The rheological characteristics of the gel

samples were determined on a Rheotest-2 device with a cone-plate assembly at a temperature of 23±0.2°C and a shear rate from 1350 s^{-1} to 4860 s^{-1}. Dropping point was tested as per ASTM standard D-566-02. Thermoanalytical investigation of samples was provided using Differential Scanning Calorimetry (DSC) method using the DSC 822^e calorimeter (Mettler Toledo) at scanning rate 0,08 $K.s^{-1}$.

Results

Synthesis of polyureas was carried out in a glass three-necked flask equipped with a stirrer and a thermometer in the following way: amines were added to the solvent or oil medium and mixed thoroughly, then diisocyanate was added with the aid of a dropping funnel within 10-15 min with stirring. At the end of diisocyanate adding, the temperature of the medium was increased to 55-65° C. Afterwards an exposure time of 2 hours at 70-80°C with stirring was given. We used the relationships between the components listed in (Table 1).

sample	dispersion medium	Component molar ratios				Mass fraction of polyurea in dispersion medium, %
		TDI	IPDI	Ethylene diamine	α-octyl amine	
PM-1-1	toluene	0.4	0	0.21	0.40	10
PM-1-2	VM-6	0.4	0	0.20	0.40	15
PM-2-1	toluene	0.42	0	0.29	0.29	10
PM-2-2	VM-6	0.42	0	0.29	0.29	15
PM-3-1	toluene	0	0.4	0.20	0.40	10
PM-3-2	VM-6	0	0.4	0.20	0.41	15
PM-4-1	toluene	0	0.42	0.29	0.29	10
PM-4-2	VM-6	0	0.42	0.29	0.29	15

Table 1: The relationship between components in the synthesis of polyureas.

The obtained reaction mixture of the "polyurea-oil" type demonstrated properties of suspension with high viscosity. It was preliminarily ground by means of a laboratory planetary ball mill "Activator-2S" (manufactured by LLC "Plant of Chemical Engineering", Novosibirsk). The grinding was carried out for a predetermined time period with 2.8 mm diameter balls made of zirconia stabilized with yttrium. The rotation speed of the drum was 20 rpm. The drum was filled with oil and balls by 45% in a ratio of 5:1. After preliminary grinding, the reaction mass was heat treated at 150-180°C for 1 hour and the milling was repeated in the above-mentioned mode for a predetermined time. A study of the obtained gel samples of polyurea-oil systems was carried out to obtain rheological, physical and spectroscopic characteristics.

Polyurea synthesized in the toluene medium was precipitated from the medium by using octane as a precipitant. After subsequent drying at 80°C within 6 h, the resulting polyurea was mixed with the oil in the same ratio as for the oil synthesis (15% mas.) and pretreated according to the conditions indicated above.

Discussion

The design of the optimal structure of the polyurea molecule is determined by the molar ratios between components of the reaction mixture. Indeed, in the most general form, the reaction of the $H_2NR_2NH_2$ diamine and the $R_3(NCO)_2$ diisocyanate leads to the polyurea formation. Use the molar ratio diisocyanate: diamine W=1:2 leads to formation of the final reaction product with the following structural formula:

$$H_2N\text{-}R_2\text{-}NH\text{-}CO\text{-}NH\text{-}R_3\text{-}NH\text{-}CO\text{-}R_2\text{-}NH_2$$

The theoretical molecular mass of such product for the used diisocyanates and diamines may be in the diapason of 280-320 g/mol depending on the used type of initial reactants. A higher molecular mass of the obtained product can be achieved using the following diisocyanate: diamine molar ratio: W=n/(n+1), where n is the number of diisocyanate moles and n+1 is the number of diamine moles. In this case, the calculated molecular mass of polyurea should be equal to:

$$M=n.M_{di}+(n+1).M_{da},$$

where M_{di} and M_{da} are the molecular masses of a diisocyanate and a diamine, respectively. In any case, the resulting product has terminal amine groups, which influence on the formation of stable gels in oil or other dispersion media should not be underestimated [7]. Polyureas products without terminal amine groups can be formed by using monoamines R_1NH_2 for the reaction with diisocyanates:

$$R_1\text{-NH-CO-NH-}R_3\text{-NH-CO-}R_1$$

This structure can be more favorable for the thermodynamic affinity to the oil base of greases due to the length of the hydrocarbon radical R_1 forming a lyophilic fragment of polyurea molecule that leads to the better colloidal stability of the polyurea-oil suspensions. A number of polyurea samples with controlled molecular mass without terminal amine groups was synthesized using mixtures of monoamines and diamines. The general structure of these products corresponds to the following formula:

$$R_1\text{-(NH-CO-NH-}R_3\text{-NH-}R_2\text{-NH-)}_n\text{-}R_3\text{-NH-CO-NH-}R_1$$

In this case, the calculated mass of polyurea should be equal to:

$$M=n.M_{di}+(n-1).M_{da}+2M_{ma}$$

where M_{ma} is the molecular weight of a monoamine.

Specific relationships between the reaction components are given in Table 1.

The polyureas synthesis was provided with particular attention to the completeness of isocyanate groups conversion, since the produced polyurea formed conglomerates up to 100μ in size. These conglomerates contain unreacted isocyanate groups even after preliminary grinding (absorption bands at the wave number 2270 cm^{-1}, (Figure 1). Therefore, after preliminary grinding, a heat treatment was carried out at 150°C for 1 hour. This treatment allowed to complete the conversion of free isocyanate groups (Figure 1) and stabilize the obtained samples of polyurea greases.

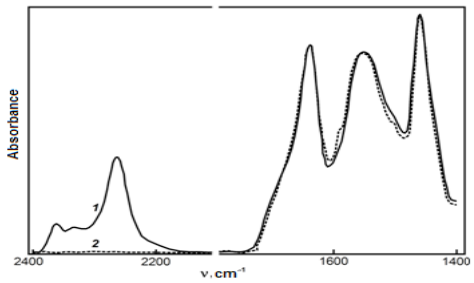

Figure 1: FTIR-spectra of the PM-1-2 sample before heat treatment at 150°C (curve 1) and after it (curve 2).

The grinding process was carried out for a variable period of time. As was established, grinding within 5 minutes leads to particles formation with size of 40-50μ (Figure 2), the particles are unevenly distributed in the dispersion medium. Grinding within 10 minutes leads the decrease in the particle size down to 15-20μ. The further grinding (15 minutes) leads to the size less than 10μ, the particles are distributed evenly. The particles size does not change after 20 minutes of processing. Therefore, the chosen grinding time was equal to 15 minutes.

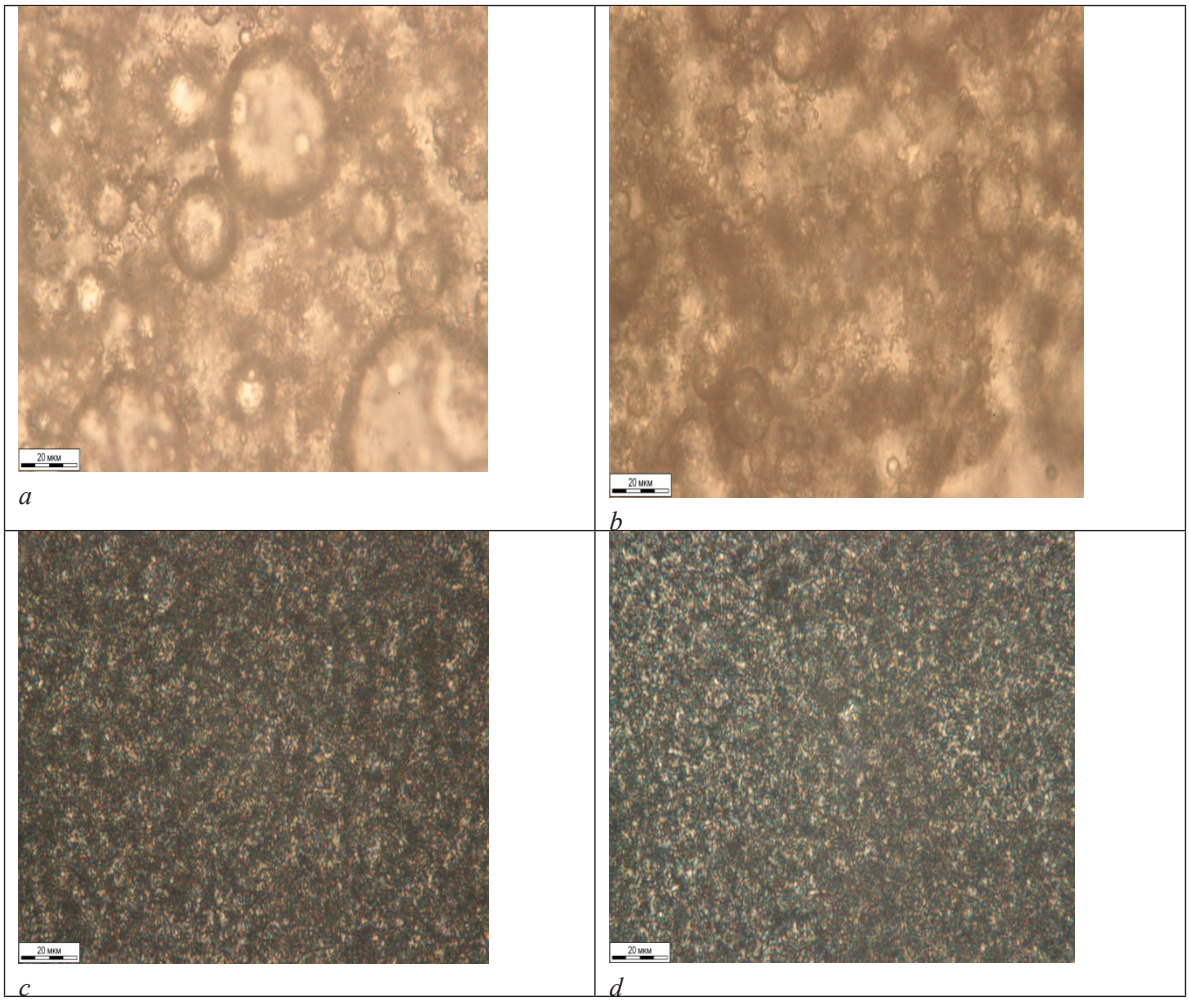

Figure 2: Images of the PM-1-2 sample after processing in the ball mill: a –5 min, b- 10 min, c- 15 min, d- 20 min.

It should be noted that samples of obtained greases synthesized in an oil or solvent environment differ somewhat in structure after grinding by the same regime (Figure 2,3).

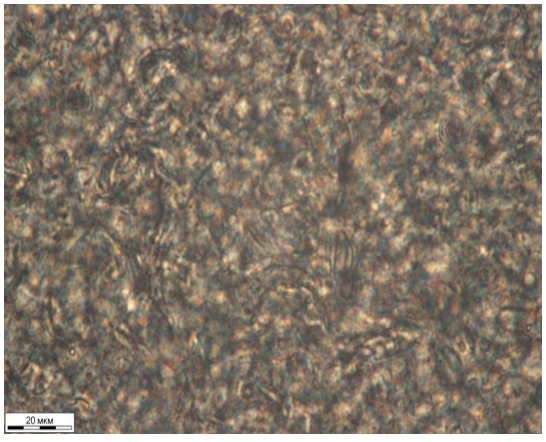

Figure 3: Image of the PM-2-1 sample after processing in the ball mill within 20 min.

As can be evidently seen, the characteristic size of the PM-1-2 sample (5μ) is larger in two times than that of PM-2-1. However, such a difference does not have a noticeable effect on the functional properties (Table 2), which confirms the optimality of the selected treatment regime.

Sample	Theoretical molecular mass	Dynamic viscosity at a shear rate 810 s^{-1}, Pa·s	Drop temperature, °C
PM-1-1	666	0.51	214
PM-1-2	666	0.51	213
PM-2-1	900	0.8	234
PM-2-2	900	0.8	232
PM-3-1	762	0.61	148
PM-3-2	762	0.57	147
PM-4-1	1044	0.9	157
PM-4-2	1044	0.86	155

Table 2: Properties of thickener samples.

The media of polyurea synthesis did not significantly affect the viscosity of the obtained greases; small discrepancies were observed only for samples PM-3-1 and PM-3-2, as well as for PM-4-1 and PM-4-2 (Table 2). A similar result was obtained for the drop temperature. In our opinion, this result correspond to the non-polar nature of the dispersion medium in both synthesis variants.

It should also be noted that the viscosity behavior of all grease samples was non-Newtonian (Figure 4). The high value of the dropping point (up to 234°C) allows using the described systems as the base of high-temperature lubricants.

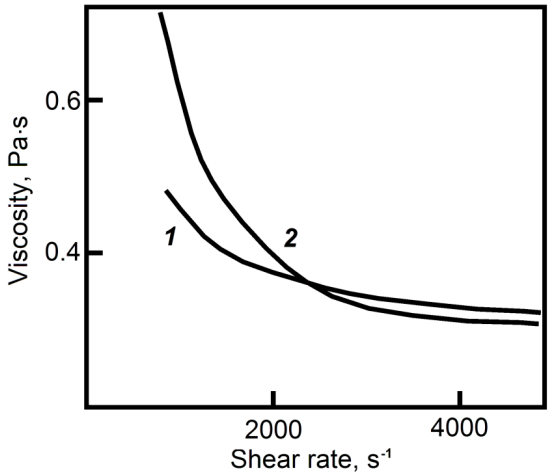

Figure 4: The viscosity versus share rate dependence at 23°C for PM-1-2 sample (curve1) and PM-2-2 one (curve 2).

It was estimated that all grease samples demonstrated a high colloidal stability during storage for 3 months (25°C). A study of the behavior of grease samples at elevated temperatures showed that the thermal stability of the samples based on IPDI are significantly lower than that based on TDI. Heating PM-1 and PM-2A greases up to 150°C leads to their rupture due to softening of the polyurea, which is confirmed by the DSC calorimetry data (Figure 5). Similar results were previously obtained for softening points of polyurethane ureas elastomers synthesized on the basis of this diisocyanates [13]. On the other side, it is known that the drop point of polyurea greases synthesized on the base of aliphatic hexamethylene diisocyanate is lower in 23° than for analogous based on toluene diisocyanate. This fact confirms an important advantage of aromatic diisocyanates for the synthesis of polyurea greases.

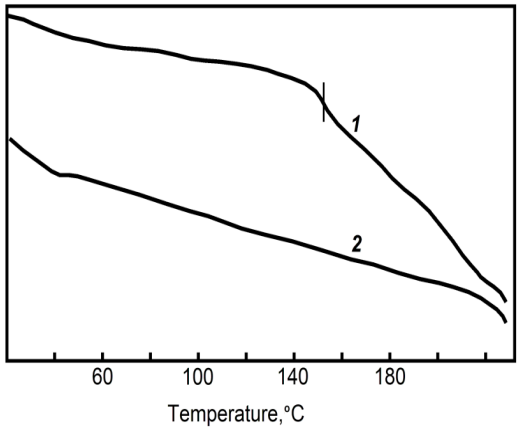

Figure 5: DSC-thermogramms for PM-3-1 sample (curve 1) and PM-1-1 one (curve 2).

Conclusions

The features of polyurea synthesis in various hydrocarbon media were studied. It was estimated that use of toluene as a dispersion medium can be applied for manufacture of polyurea thickeners using the stage of polyurea powder thickener synthesis. These products can be easily ground and allow producing greases not only with mineral oils, but also with other liquid media for perspective lubricants. The better Thermostability of polyurea greases on the base of toluene diisocyanate can be explained using comparative thermodata.

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