Polyurethane Synthesis Reactions in Asphalts

ANDRZEJ BUKOWSKI and JACEK GRĘTKIEWICZ, *Warsaw Technical University, Branch at Płock, 09-400 Płock, Poland*

Synopsis

A series of asphalt–polyurethane composites was prepared by means of polyurethane synthesis in asphalt and carried out in melt. The applied materials were asphalts of differentiated group components content, polyester polyols of chain structure from linear to strongly branched, 2,4-tolylene diisocyanate, 4,4-methylenebis(phenyl isocyanate), and tinorganic catalyst. The asphalt components react with isocyanates to a minimal degree. The influence of the applied substrates, temperature, and polyurethane content in the system on the basic kinetic relations characterizing the process is presented. Polyurethane synthesis in asphalts does not differ in a fundamental way from the obtaining of polyurethanes, especially when their content in the composition is significant, 20 wt % and more.

INTRODUCTION

Plastics in the form of composites are widely applied in different technical branches.[1] Lately, the application of numerous polymers for modification of asphalts and obtaining of asphalt–polymeric composites is known.[2] In recent years, thermoplastics (mainly polyolefines) have dominated in these applications, but not long ago, polymers like epoxy resins and polyurethanes (PU) have come into use.

Articles on asphalt–polyurethane composites deal with the practical aspects of obtaining and applying them, and that is why they are patents mainly,[4–10] of which a few were quoted as examples. It has therefore been decided to investigate kinetic relationships characteristic of obtaining PU in asphalts in order to increase the existing scope of knowledge. Systems of that type are complicated objects of investigations, as the creation of composite structures, takes place simultaneously with the growth of polymer chain while obtaining such systems.[11]

Asphalts themselves are mixtures of different chemical compounds, and in regard to physical structure they are treated as colloidal-dispersion systems consisting of at least two phases. Among the compounds that constitute asphalts, the most characteristic are polycyclic hydrocarbon compounds containing also oxygen, nitrogen, and sulfur.[2,12]

EXPERIMENTAL

Materials

Syntheses of PU were carried out in Polish asphalts PS-40/175 D-35 and PK-70 produced from Rhomaskino crude oil. These asphalts have different group component contents (Table I) which are reflected in their colloidal structure. The first kind of asphalt can be considered a model of the sol type, the second of the sol-gel type, and the third of the gel type.

TABLE I
Properties of Asphalts Applied in the Investigations

Properties	Type of asphalt		
	PS-40/175	D-35	PK-70
Softening point according to R. and B. method, °C	40.5	51.5	77.2
Group components content, wt %			
Asphaltenes	14.6	18.2	26.9
Resins	40.8	36.8	27.9
Oils	44.6	45.0	45.2

Polyester polyols from Zachem named Poles have been applied as polyol components for the obtaining of PU (Table II). The applied isocyanates were 2,4-tolylene diisocyanate (2,4-TDI) from Merck AG and 4,4-methylenebis(phenyl isocyanate) (MDI) from Bayer AG. Also, tinorganic catalyst S-26 produced by Acima was used.

Method of Synthesis

Syntheses were carried out in typical laboratory glass sets for polyreactions in melt. For all compositions, —NCO/—OH = 1 was accepted.

At the beginning, asphalt and polyol were heated at 120°C and under $p = 0.7$ kPa, with constant stirring. Next, isocyanate was added. After 3.5 h, the mass was poured out to a metal container, which was placed in the oven at the same temperature at which the process was conducted, for 6.5 h.

Analyses

For determining the acid and hydroxyl numbers of asphalts, the best repeatability and precision of the results were obtained with methods given in Gun's monograph.[12]

During the course of PU synthesis in asphalt, samples were taken after 5, 15, 30, 60, 90, 120, 150, 180, 210, and 600 min after the addition of isocyanate and also after 30 days of storage of the compositions at 25°C. The content of unreacted isocyanate was determined in the samples according to the ASTM D 2572 method.

From the experimental data, the degree of conversion $d\epsilon_i$ and the mean rate of reaction were calculated. The constant rate of the reaction was calculated from the Yerofiev–Avramov equation

$$K\tau = [-\ln/1 - d\epsilon_i/]^{1/n}$$

where τ is time in minutes.

TABLE II
Properties of Poles Polyester Polyols

Properties	Type of poles		
	40/21	60/22	300/8
Chain structure	linear	slightly branched	strongly branched
Hydroxyl number, mg KOH/g	39.5	59.2	241.4

The composition samples in the form of foil after 30 days from their preparation were spectroscopically investigated in IR for the presence of free —NCO groups, which showed a sharp absorption band at 2280 cm^{-1}.[13]

RESULTS AND DISCUSSION

Reactivity of Asphalts

It could be assumed that in a three-component reaction mixture, apart from the basic reaction during which PU arises, a chemical reaction between isocyanate and the asphalt components containing active hydrogen in such groups as —OH, —COOH, —SH, $>$NH takes place.

In order to determine the reactivity of asphalts with isocyanates, two methods were chosen. The first was the designation of asphalts for the evaluation of their potential reactivity. The second method was based on the reaction between asphalts and 2,4-TDI, with the second component content equal to 20 wt % PU. The reaction was run at 90°C for 10 h with constant stirring.

The results from both methods based on the amount of 2,4-TDI spent in the reaction on the mass of given asphalt are shown in Table III. While comparing the results obtained by means of the two methods, a close relationship can be observed. These values indicate that, with slight simplification, the effect of isocyanate groups with asphalt components can be ignored as not valid.

Reactions in Different Asphalts

The systems with initial substrates content equal to 20 wt PU, on the basis of Poles 60/22, and 2,4-TDI, prepared at 90°C, were examined. The results are shown in Figure 1. The times of reaction pointed out for $d\epsilon_i = 0.5$ are included in the range of 45–75 min. The applied asphalts vary the reaction course in a limited scale; the curves for asphalts D-35 and PK-70 are very close to each other. A different relationship for asphalt PS-40/175 can be explained by its considerably smaller viscosity in comparison with the other asphalts. After 10 h of reaction, the degree of conversion for the examined systems was 0.94–0.98. After 30 days of storage, the presence of unreacted —NCO groups was not stated.

It is known that the reaction of PU synthesis in solution and melt is autocatalyzed by the arising product in the range of adequately high values of conversion. It results in the growth of a constant rate of reaction together with conversion growth.[14,15]

This phenomenon also takes place in the case of synthesis of PU carried out in asphalts (Fig. 2). The course of reactions in asphalts and toluene was com-

TABLE III
Results of Determined Reactivity between Applied Asphalts and Isocyanate

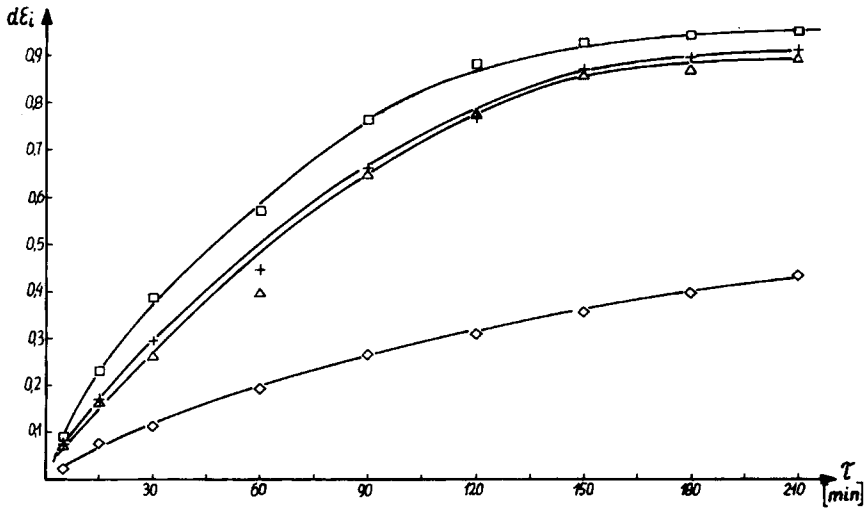| Properties	Type of asphalt		
	PS-40/175	D-35	PK-70
Consumption of 2,4-TDI calculated from acid and hydroxyl numbers, 10^{-4} g/g	6.05	3.88	5.58
Consumption of 2,4-TDI determined from the course of reaction 10^{-4} g/g	10.26	6.50	9.22

Fig. 1. Relationship between degree of conversion and time of reaction for different asphalts and toluene: (□) PS-40/75; (+) PK-70; (△) D-35; (◇) toluene.

pared. From the data presented in Figure 1, it is evident that the progress of the process becomes faster when carried out in asphalts than when toluene is used as a solvent. Considering the results of this stage of investigation, it was decided to use only asphalt D-35.

Reactions with Different Isocyanates

For the conditions mentioned above, reactions in asphalt D-35 with the use of 2,4-TDI and MDI were carried out. The features of $d\epsilon_i$ changes in time are the same for both isocyanates being compared. Values of $d\epsilon_i$ for particular times are approximately the same, with somewhat smaller values for MDI. 2,4-TDI
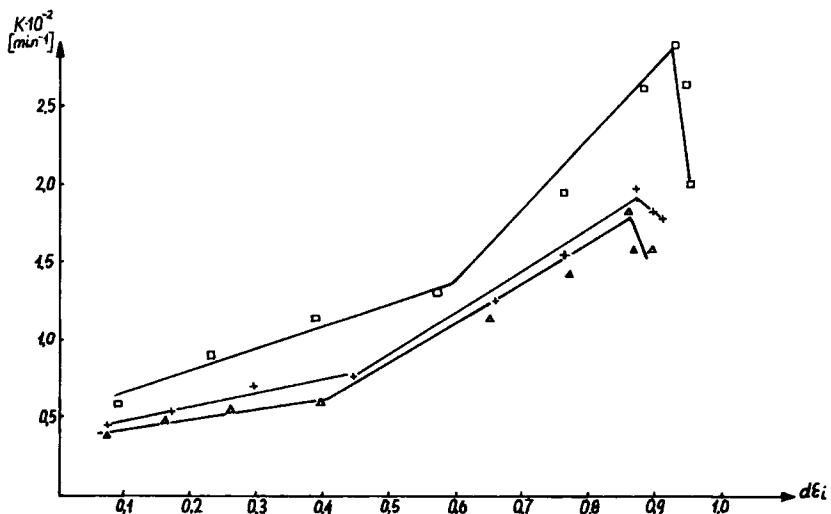

Fig. 2. Relationship between constant rate of the reaction and degree of conversion, with use of different asphalts: (□) PS-40/175; (+) PK-79; (△) D-35.

has been chosen for further investigations because of its more frequent application in PU synthesis.

Reactions with Different Polyester Polyols

The purpose of this stage was to determine the influence of the polyester polyol structure on the course of the reaction in question. After the assignation having been accepted in previous stages, systems consisting of asphalt D-35, 2,4-TDI, and Poles 40/21, 60/22, and 300/8 were examined. Initial substrates for the synthesis of PU constituted 20 wt % of the system; the reaction took place at 90°C.

Figure 3 presents the dependence $K = f(d\epsilon_i)$. During working out the obtained kinetic data, attempts were made to apply kinetic equations taken from the literature, to obtain a linear dependence. After having tested 18 different equations, dependences approximately linear were obtained only for the Yerofiev–Avramov equation with $n = 2/3$, in the form of broken lines, which proved the presence of different synthesis stages. While analyzing the relationship between $d\epsilon_i$ and the hydroxyl number, it was noted that in the first stage of reaction ($\tau = 0$–120 min), the lowest conversion was achieved by the system with Poles 40/21. But in further stages the progress of the degree of conversion for this system was the greatest. None of the systems examined spectroscopically and chemically displayed the presence of unreacted isocyanate.

For further investigations, Poles 60/22 has been chosen because of its intermediate structure in comparison with the rest of used polyols.

Reactions with Different Content of Substrates

In the systems containing asphalt D-35, Poles 60/22, and 2,4-TDI, the contents of the components have changed to obtain systems of PU content 10, 15, 20, and 40 wt %. It is clear from Figure 4 that with small PU content (10–15 wt %) the dependences have a linear character while with greater PU content they are broken lines that consist of two (40 wt %) or three (20 wt %) intervals. It proves
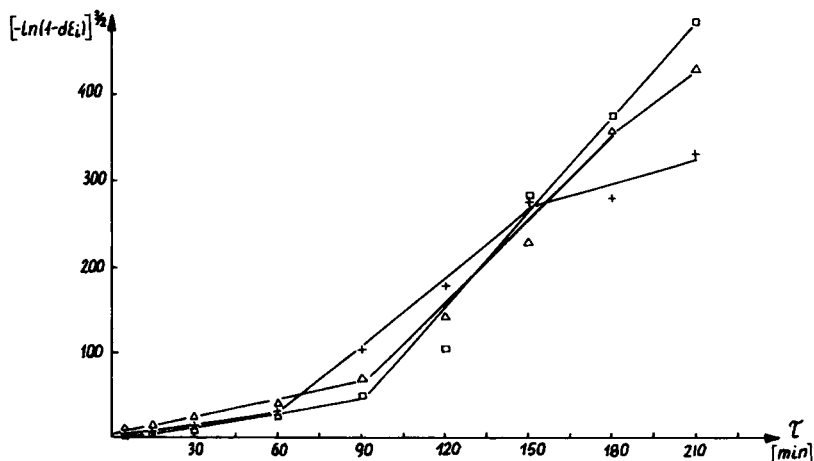

Fig. 3. Relationship between degree of conversion and time after application of Yerofiev–Avramov equation for different polyester polyols: (□) Poles 300/8; (+) Poles 60/22; (△) Poles 40/21.
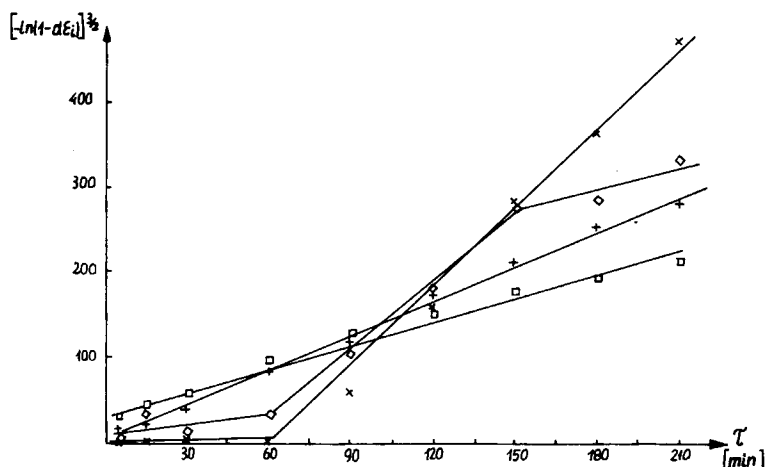
Fig. 4. Relationship between degree of conversion and time of reaction for different contents of polyurethane in system, after application of Yerofiev–Avramov equation: (□) 10%; (+) 15%; (◇) 20%; (×) 40%.

the lack of autocatalysis at small amounts of PU; however, if the content of PU is greater, autocatalysis takes place.   Mean reaction rate decreases as the reaction proceeds and the reaction for 40 wt % PU content has the highest rate.

In the initial stage, the highest degree of conversion is obtained with compositions with the lowest PU content; and in the following stages, the reverse situation takes place.   After 10 h of reaction and for 10 wt % PU, $d\epsilon_i = 0.91$; and for 40 wt %, $d\epsilon_i = 0.96$.   The systems do not indicate the presence of —NCO groups analogously to previous tests.

The acquired data indicate that with PU content greater than 15–20 wt % in the system, the course of polyaddition reaction is similar to its course in the case of PU preparation in melt or in solution.

Reactions at Different Temperatures

The system consisting of asphalt D-35, Poles 60/22, and 2,4-TDI with 20 wt % PU was examined during the reaction at 70, 80, 90, 100, 110, and 120°C.

Figure 5 shows that the degree of conversion of substrates increases with temperature, especially so at temperatures above 90°C.   It is characteristic that only for 120°C the dependence obtained was in straight-line form. It is confirmed by the $d\epsilon_i$ values after 10 h of reaction, which vary from $d\epsilon_i = 0.879$ at 70°C to $d\epsilon_i = 0.997$ at 120°C.

From the dependence $\lg K = f(1/T)$, the activation energy E_A was calculated. Because the synthesis of PU is a multistage process, the values of E_A for the spontaneous reaction ($d\epsilon_i = 0.3$) and the autocatalyzed reaction ($d\epsilon_i = 0.7$) were calculated.   The values obtained are respectively 64 and 43 kJ/mol, and they confirm the presence of autocatalysis in the last stages of the reaction.

Reactions with Catalyst

For the above-mentioned system prepared at 90°C, the addition of tinorganic catalyst S-26 in amounts of 0.05, 0.1, and 0.25 wt % of the system was applied. For the materials examined the most favorable quantity of catalyst is about 0.1 wt %.
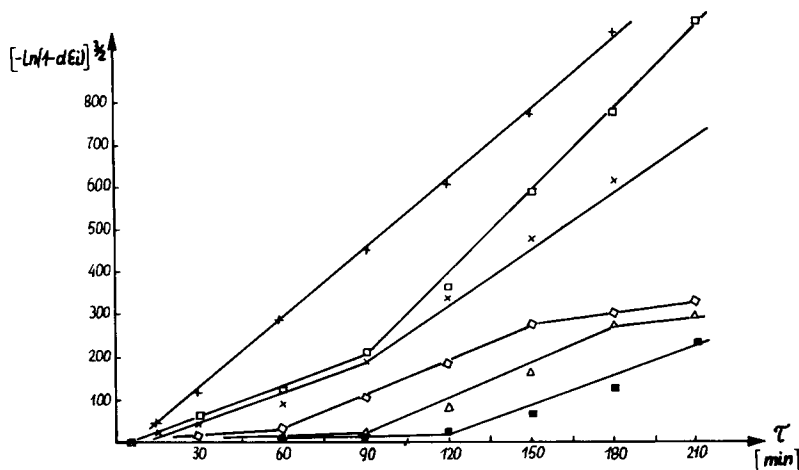
Fig. 5. Relationship between degree of conversion and time of reaction for different temperatures of reaction course, after application of Yerofiev–Avramov equation: (+) 120°C; (□) 110°C; (×) 100°C; (◇) 90°C; (▲) 80°C; (□) 70°C.

Mean reaction rates were several times greater than in the uncatalyzed system. Also the times for $d\epsilon_i = 0.5$ are in the range of 6–20 min. The effect of catalysis on the reaction course in the case of asphalt–polyurethane systems is thus apparent.

CONCLUSIONS

The conducted investigations have proved that synthesis of PU carried out in petroleum asphalts do not differ significantly as far as the kinetic relations describing their course are concerned than in the case of obtaining PU. This is in accordance with the proved lack of essential chemical action between the components of asphalts and isocyanate groups.

In systems with low PU content, i.e., to 20 wt %, the characteristic effect caused by autocatalysis of the arising product does not appear. The obtained results indicate that as far as the selection of conditions and methods of reaction course for preparation of asphalt–polyurethane composites is concerned, one can rely on dependences known in the chemistry and technology of polyurethane. It is of great value for the production and practical application of the materials in question.

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