Investigations on copolymerization reaction in melted asphalt

Andrzej Bukowski and Blandyna Osowiecka
Institut of Chemistry, Płock Branch of Warsaw Technical University, 09–400 *Płock, Łukasiewicza* 17, *Poland*
(*Received* 19 *May* 1980)

The results of the investigations on copolymerization reaction of unsaturated polyesters with styrene initiated with radicals in a melted asphalt medium are presented in this paper. The optimal parameters for the reaction and the role of asphalt in this reaction have been defined. It has been found that a radical copolymerization reaction in a monophase system can be conducted in melted asphalt medium and its course is dependent on the type of asphalt and type of initiator. The results of the investigations show that asphalt is an inhibitor of copolymerization reactions initiated with radicals.

INTRODUCTION

Preparation of macromolecular compounds during reaction course *in situ* in an asphalt medium is one of the methods of improving its properties. This method is applied, in practice, except for commonly used physical modification in which the modification agent (polymer) improves the asphalt properties, being chemically inactive to asphalt.

A number of literature sources describe the various possible types of polyreaction course (polymerization, polycondensation, polyaddition) in the melted asphalt medium[1–4]. The works discussing this problem do not define explicitly the part of asphalt involved in these reactions, instead they concentrate mainly on the technological aspects. The asphalt components that take part in the polyreaction processes in melted asphalt have not yet been scientifically proved.

Difficulties in studying these interesting problems are due to the complex and not fully recognized chemical structures of asphalts. They are complex mixtures of aliphatic cyclic and heterocyclic hydrocarbons with a significant participation from condensed aromatic ring structures joined by short bridges in which heteroatoms such as oxygen, nitrogen and sulphur are present. Oxygen occurs also in hydroxylic and carboxylic groups identified in some asphalt components.

Asphalts have a colloidal structure and are sparingly soluble macromolecular compounds with condensed aromatic ring structures in a dispersive phase. Oil components containing alkanes and cycloalkanes are in a dispersive phase while the stabilizing agents of the colloidal system are asphaltic resins represented mainly by cycloparaffins and aromatic hydrocarbons. Asphalt properties are closely connected with the content and chemical structure characteristics of these components.

The complexity of the subject, lack of fully investigated theroetical and practical aspects, motivated the undertaking of the investigations on copolymerization reactions of unsaturated polyesters with styrene in a melted asphalt medium which includes radical polyreactions.

The available literature[5–8] deals mainly with practical aspects and is limited to giving recipes and methods of preparing such compositions with improved physicochemical properties.

The aim of our investigations was to work out the optimal parameters for the copolymerization reaction of unsaturated polyester with styrene in a melted asphalt medium and an attempt determining the part asphalt plays in this reaction.

EXPERIMENTAL

The experimental part of this paper was conducted in 4 stages:

(i) Determination of optimal parameters of the copolymerization reaction in the melted asphalt medium.

(ii) Testing the activity of commonly applied radical initiators in relation to resin crosslinking in the ashpalt.

(iii) Determination inhibiting influences of asphalts on the radical reaction according to their amounts in the cured system.

(iv) Attempt to define the role of asphalt in the copolymerization reaction of unsaturated polyester with styrene.

Asphalt properties are given in *Table 1*.

Polimal 109, the resin of general application obtained from anhydrides of maleic and phthalic acids and from

Table 1 Asphalts properties determined due to Polish standards

Determined properties	Type of asphalt			
	Road		Industrial	
	D–35	D–100	P–50	P–70
Softening point according to *R* and *B* method	56.0	46.5	53.0	71.0
Fragility point (°C)	–4	–9	–1	+6
Penetration at 25°C (°P)	35.0	104.0	46.0	14.5
Ductility at 25°C (cm)	65.2	>100.0	90.0	5.5
Group components content (wt %)				
– oil	46.8	41.2	39.5	45.4
– resins	39.4	45.1	40.1	27.9
– asphaltenes	17.5	13.5	20.0	26.9

0032-3861/81/101415-04$02.00

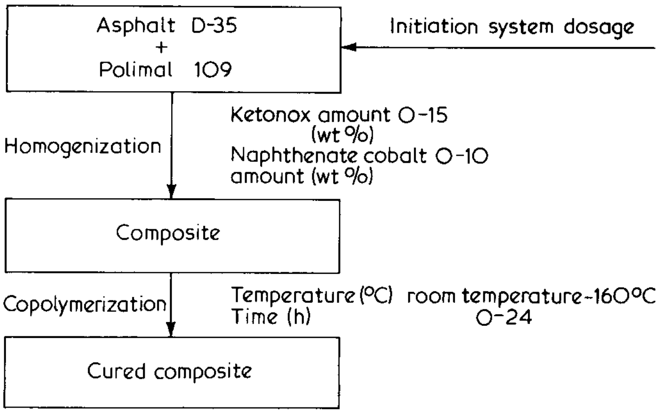

Figure 1 Block diagram of the investigations into copolymerization process of unsaturated polyester with styrene in the melted asphalt medium

Table 2 Results of the investigations on the curing temperature influence on the composites properties

Determined properties	Curing temperature (°C) 22–25	50	80*	100	140	160
Softening point *R* and *B* (°C)	<30	31	47	51	55	61
Degree of styrene conversion (wt %)	–	41.0	54.6	70.0	79.0	86.0
Degree of resin cross-linking (wt %)	–	29.5	49.0	52.0	68.0	72.0

* Temperature of initiator decomposition

ethylene glycol, was used. The resin contained ~30 wt% of styrene.

The following initiators were used for radical copolymerization initiation of unsaturated polyester with styrene:

(a) Hydroperoxide of methyl-ethyl ketone (Ketonox), 50% solution with methyl phthalate, content of 6.6 wt% of active oxygen.

(b) Cyclohexanone hydroperoxide (Heksanox) is a suspension in di-butyl phthalate stabilized with polyvinyl chloride (PVC) containing 6.2 wt% of active oxygen.

(c) Cumene hydroperoxide (CHP), the compound was chemically pure with a content of 5.2 wt% of active oxygen.

(d) Benzoyl peroxide (BP), chemically pure, containing 2.9 wt% of active oxygen.

A block diagram of the first stage of the investigations into the copolymerization process of unsaturated polyester with styrene in a melted asphalt medium is given in *Figure 1*.

The following method of obtaining and curing asphalt–resin composites was adopted: the asphalt and polyester resins were homogenized at a temperature ~50°C higher than the softening point of asphalt, and then the initiator and accelerator were added. This hot melt was poured into the covered crystallizers and heated in a laboratory dryer in the previously described temperature and time conditions. The results of the investigations are presented in *Tables 2* and *3* and in *Figure 2*.

Investigations on defining the optimal parameters for unsaturated polyesters crosslinking with styrene in the melted asphalt medium showed that the restraining influence of asphalt on the crosslinking process is dependent on temperature, time and also on the amount of initiator used for the reaction initiation. Together with the rise in temperature and curing time and also with the increase in the amount of initiator used for the reaction initiation a gradual reduction in the restraining influence of asphalt can be observed. Application of accelerator in the reaction conditions (high temperature) has no influence on homolytic dissociation of peroxide.

The optimal conditions for resin crosslinking in asphalt are as follows: (1) initiator additive (Ketonox) 2–10% wt% in relation to the resin; (2) crosslinking temperature >100°C; (3) curing time of 3–5 h.

The second stage included analogical investigations of other initiators chosen from those commonly used for curing polyester resins. Investigations were also carried out to discover the best initiator for reaction initiation in the asphalt. 35 wt% of Polimal 109 added to the asphalt (asphalt D–35) was crosslinked and the curing conditions were adopted as the standard conditions in the first stage of the investigations. The results of the investigations are presented in *Table 4*.

In defined conditions the activity of the discussed initiators, in relation to the tested resin crosslinked in the asphalt, is dependent on their chemical character and activity. Decarboxylation of oxybenzoyl radicals. obtained from peroxide decomposition, can be responsible for lowering the efficiency of the benzoyl peroxide operation as the source of radicals. The presence of phenyl radicals instead of oxybenzoyl radicals can limit the process of radical reaction initiation. Out of the initiators applied in the studied conditions cumene hydroperoxide (CHP) was useful for the reaction initiation in asphalt although its efficiency of operation is lower than that of Ketonox.

Table 3 Softening point *R* and *B* (°C) of composites cured at various temperatures

Curing time (h)	Curing temperature (°C) 50	100	140
1	27.5	44.0	50.5
2	29.0	51.0	51.0
3	28.0	53.0	52.0
4	36.0	52.0	57.0
5	36.5	53.5	57.0
24	38.0	56.0	61.5

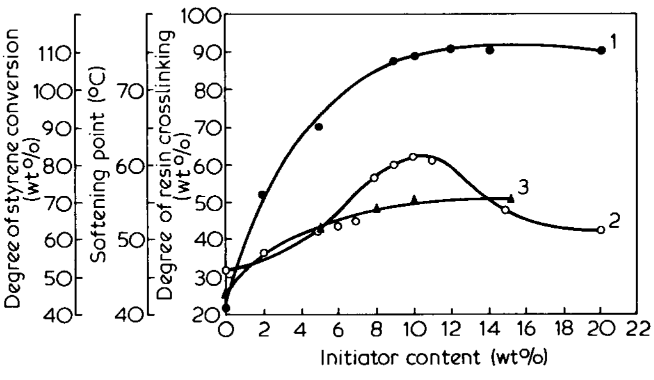

Figure 2 Dependence of degree of resin crosslinking (1); softening point (2); and degree of styrene conversion (3) on initiator content

Table 4 Properties of asphalt–polyester composites cured with cumene hydroperoxide (CHP) cyclohexanone hydroperoxide (Ketonox) and benzoyl peroxide (BP)

	CHP		Hexanox		BP	
Initiator amount in relation to resin (wt %)	Softening point (°C)	Degree of resin crosslinking (wt %)	Softening point (°C)	Degree of resin crosslinking (wt %)	Softening point (°C)	Degree of resin crosslinking (wt %)
2	39.5	58.5	<25	9.5	28.0	–
5	47.5	58.0	26.0	19.0	29.0	10.0
8	51.0	60.5	28.5	35.5	30.0	13.0
10	53.0	68.5	43.0	45.0	31.5	19.0
13	56.5	67.5	42.0	49.5	32.5	24.5
15	59.5	70.5	51.0	52.0	43.0	31.0

Table 5 Results of cured composites properties based on asphalt D–35 and Polimal 109

Polimal 109 amount in reaction system (wt %)	Softening point (°C)	Styrene conversion (wt %)	Degree of resin crosslinking (wt %)
–	56.0 ± 1.0	–	–
5	56.5 ± 1.5	–	–
10	56.5 ± 2.0	12	0.2
15	58.0 ± 2.0	21	16
20	59.0 ± 1.5	39	27
25	59.5 ± 2.0	43	37
30	61.0 ± 1.0	60	55
35	67.0 ± 0.5	67	71
40	71.0 ± 0.5	78	77
45	76.0 ± 0.5	85	80
50	83.5 ± 2.5	88	88
55	92.0 ± 1.5	91	92

The third stage of the investigations was aimed at determining the relationship between the asphalts restraining influence and their amounts in the system during curing in the conditions accepted as optimal from the first stage of the investigations. The results of these investigations are listed in *Table 5* and *Figure 3*.

The analysis of the results leads to the following conclusions:

(i) It is possible to run in asphalts a medium copolymerization reaction of unsaturated polyester with styrene and as a result change both road and industrial asphalt properties if the amount of resin in asphalt is above 25 wt%.

(ii) Reduction or halting of the copolymerization process of unsaturated polyester with styrene in a system where the amount of resin does not exceed 25 wt% points to inhibition.

According to literature data[10], inhibiting properties of asphalts in radical processes are due to stable free radicals present in the asphalts and also compounds containing such heteroatoms as sulphur, oxygen and nitrogen.

In the fourth stage was the determination of the content group components such as thermomechanical and rheological curves, i.r. spectroscopic studies, elemental analysis and others.

Some results of these investigations are given in *Figures 4, 5*, and *6*. The results of the investigations confirm the assumption formulated on the basis of physicochemical investigations concerning inhibiting asphalt influence on the fradical reaction. The significant flow temperature rise and the stability of the internal structure of the composites

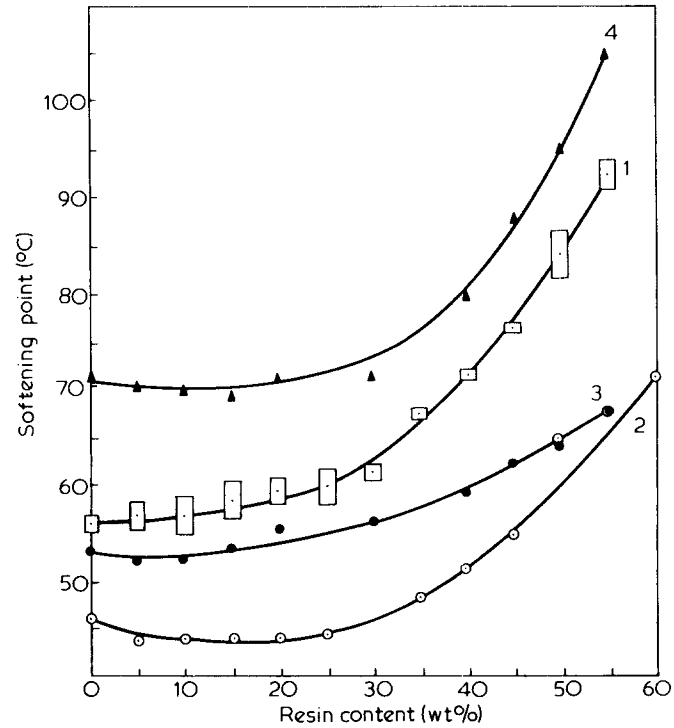

Figure 3 Dependence of cured composites softening point on the amount of polyester resin (1), D–35; (2), D–100; (3), P–50; (4), P–70

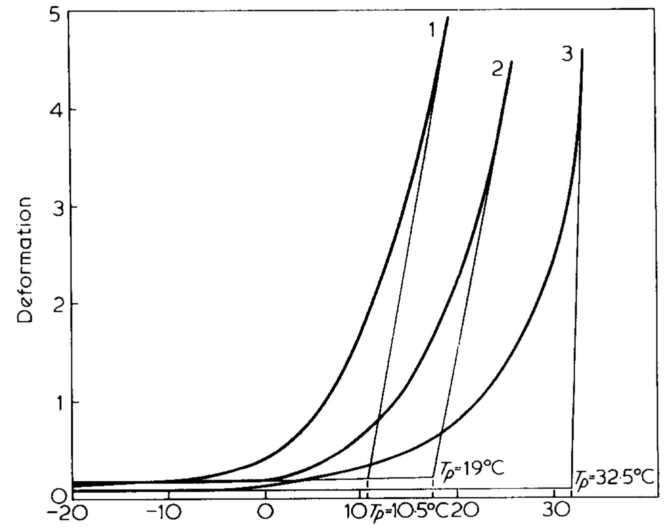

Figure 4 Thermomechanical curves: asphalt D–35 (1); cured composite containing 40 wt % polyester resin (2); 50 wt % polyester resin (3)

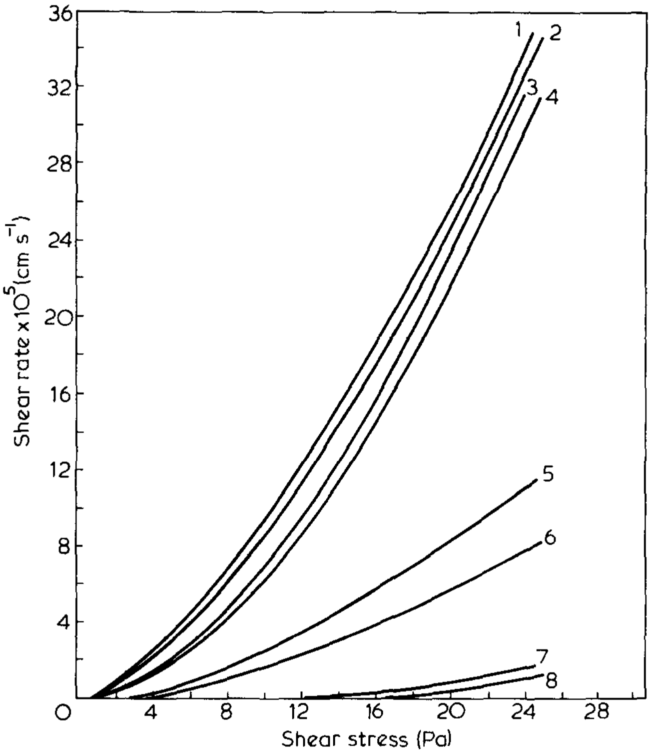

Figure 5 Flow curves determined at 20°C for asphalt D–35 and for cured composites with various Polimal 109 content (1, D–35; 2, 10% resin; 3, 20% resin; 4, 30% resin; 5, 35% resin; 6, 40% resin; 7, 50% resin; 8, 55% resin)

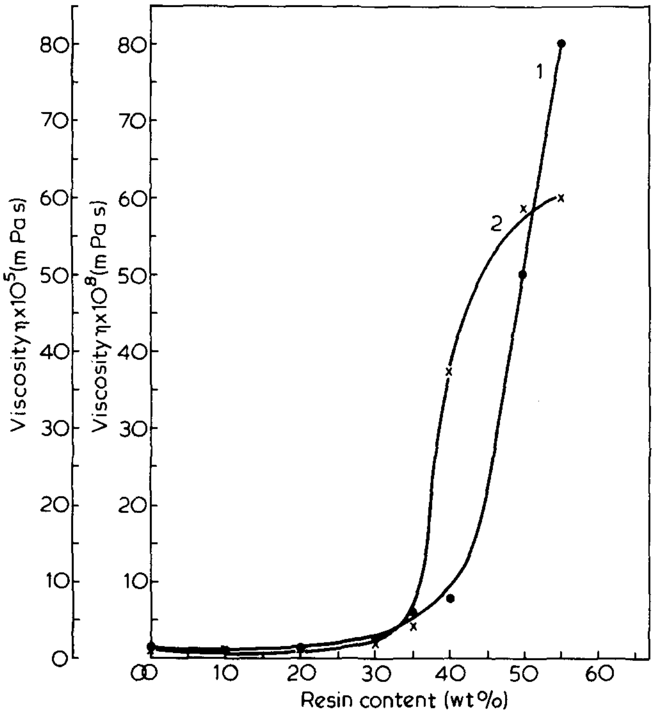

Figure 6 Relationship between viscosity of cured composites and Polimal 109 content of temperature 20°C, (1); 60°C, (2)

containing above 30 wt% of polyester testify to the inhibiting influence of the asphalt on the radical reaction. The ashpalt inhibiting operation in the copolymerization process of polyester with styrene, results from the activity of free radicals present in the asphalts, which deactivate primary radicals obtained from initiator decomposition. Moreover, sulphur compounds can also play a part as inhibitors. Out of three basic group components in asphalts, asphaltene fractions have the highest amount of free radicals and heterocompounds and because of this, asphaltenes play a most crucial role in inhibition.

The results show that because of the mutual relationship of the asphalt–polyester resins components, a microheteroorganic system is obtained which has a more stable inner structure than pure asphalt. Asphaltenes build in into the cured polyester resin network as proved by elemental analysis. Sulphur content rises from 0.05 to 0.17 wt% and nitrogen content from 0.38 to 0.78 wt% in the resin cured in asphalt due to an increase in resin content in the cured system is significant. It can be accepted that the products of radical copolymerization of unsaturated polyester with styrene in asphalt medium, is a combination of cured resin with an asphaltene fraction and it has higher resistance to temperature and chemicals.

CONCLUSIONS

It is possible to run radical copolymerization of unsaturated polyester with styrene in a monophase system if the content of polyester resin in the reaction medium does not exceed 25 wt%. The course of this reaction is dependent upon the type of asphalt and the initiator.

If the resin content does not exceed 25 wt% in the asphalt medium, the inhibiting properties of asphalts in radical processes cause the copolymerization of unsaturated polyester with styrene to run with a low efficiency. The results of the reaction course in a cured system, determined on the basis of degree of crosslinking and degree of styrene conversion reinforce this proposed inhibiting process.

The asphalts inhibiting influence is reduced because of the increased amount of radical initiator application (4–5 times in comparison with pure resin), because of a higher curing temperature (on average ~50°C higher than temperature of homolytic initiator dissociation) for a resin content from 25 to 55 wt%.

REFERENCES

1 Gundermann, E. *Bitumen, Teere, Asphalt, Peche*, 1972, **8**, 313
2 Leybourne, A. E. and Schweyer, H. E. *IEC Proc. Des. Develop.* 1962, **1**, 127
3 USA Pat. 3 547 850, 1970
4 Japan Pat. 7 467 913, 1974
5 Ger. Offen. 2 235 170, 1974
6 Ger. Offen. 2 322 250, 1974
7 Depke, F. M. Bitumen und Teerlacke, Berlin WA Colomb 1970
8 USA Pat. 3 287 296, 1966
9 Rado, R. Polymer reactions initiated with peroxides, Warsaw WNT, 1974
10 Gundermann, E. *Strasse* 1975, **6**, 242