

A Study of the Compatibility of Synthetic Rubbers with Phenolic Resins

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Synopsis

The compatibility has been studied of two types of synthetic rubbers with two types of phenolic resins by measuring the heat effect of mixing of their equiponderant solutions in varying volume ratios. The measurements were made in an adiabatic calorimeter. On the basis of the calorimeter curves obtained in the study, compatibility has been established for all the components under investigation over a wide range of ratios. It has also been demonstrated that the method is applicable to such mixtures independent of the volume ratio of the main components.

INTRODUCTION

Solutions of polymer materials are widely used for the preparation of lacquers and adhesives. The characteristics of the polymer compositions thus obtained and of the corresponding films depend upon a variety of factors, compatibility being one of considerable importance.

The compatibility of the polymer materials is characterized by their ability to form thermodynamically stable, uniform, and monophasic systems. The compatibility can be established by means of several techniques: electronographic,¹ dilatometric,² optical,³ measuring the heat of mixings,⁴ and others.

The study of the compatibility of polymers by measuring the heat effect of mixing has had limited application and has not been fully explored yet. According to Struminski and Slonimski,⁴ the appearance of a positive or a small negative effect should be taken as a criterion of compatibility, while Gurevich and Frost⁵ suggest as a criterion the abrupt changes in the calorimetric curves, independent of the sign of the heat effect.

This paper presents the results of experiments on the compatibility between plasticized synthetic rubbers, poly(butadiene acrylonitrile) and polychloroprene, and phenolic resins, *p-tert*-butylphenolformaldehyde resin and a rosin-modified phenolformaldehyde novolak resin, used in the preparation of thermosetting adhesives by measuring with an adiabatic calorimeter the heat effect of mixing. The calorimeter used in the study was the same as described by Gurevich⁵ in which the insulating air vessel was replaced by a water thermostat.

EXPERIMENTAL

Materials

Poly(butadiene acrylonitrile) rubber, commercial product SKN-26 (USSR)

Polychloroprene rubber, commercial product Perbunan C 210 (German Federal Republic)

p-*tert*-Butylphenolformaldehyde resin, commercial product Balresin(Bulgaria)

Rosin-modified phenolformaldehyde resin, commercial product Kofenal 220 (Bulgaria)

Methyl ethyl ketone, pure, bp 80°C; sp.gr.0.800

Benzene, pure, bp 80°C; sp.gr.0.875

Methods and Equipment

Plasticizing of Rubber. A measured amount of the corresponding rubber cut to small pieces is rolled on a double-roll laboratory roller at maximum pressure and cooling of the rollers, during a period of 10 min for Perbunan C 210 and 30 min for SKN-26.

Preparation of Stock Solutions. The solutions were prepared by covering the corresponding rubber cut to small pieces or the finely ground resin with the proper amount of solvent and agitating the mixture at room temperature until a homogeneous solution was obtained.

Calorimeter and Procedure. A diagram of the equipment is shown in Figure 1. A measured quantity of the solution (enough to cover the mercury bulb of the thermometer) is placed in the vessel (b), while the second solution is poured in the container (d), which has been plugged in advance

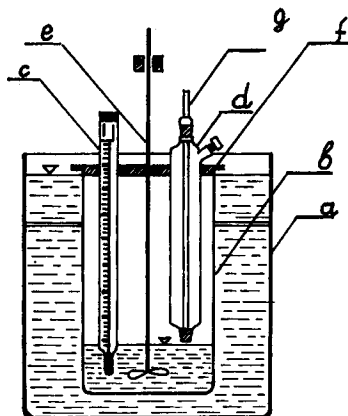


Fig. 1. Diagram of adiabatic calorimeter: (a) water thermostat; (b) glass vessel with diameter 75 mm and height 240 mm; (c) Beckmann thermometer; (d) container of diameter 40 mm, height 160 mm, and a lower outlet 7.5 mm in diameter; (e) glass agitator; (f) plastic lid 10 mm thick; (g) glass rod with ground glass tip.

with the glass rod (g). The vessel (b) is capped off with the lid (f), and the Beckmann thermometer (c), the agitator (e), and the container (d) are all mounted in place and the whole setup is placed in the water thermostat (a). The calorimeter is equilibrated at 25°C for 20–30 min with the agitator on. Next, the glass rod plugging the lower outlet of the container (d) is pulled up and the solution is allowed to flow into the container (b). The temperature is read off immediately after the mixing of the two solutions, and then readings are taken at 30-sec intervals.

RESULTS AND DISCUSSION

Two stock rubber solutions and three stock solutions of phenolic resin were used in the study. These were used for the preparation of three basic mixed solutions by taking different ratios of the stock solutions. Table I lists the characteristics of the mixtures. The table shows that the stock solutions are of the same concentration and that the final solutions are always made up to the same volume. In the experiments, the final volume after mixing the two solutions was 250 ml.

In a series of tests, a study was made of the change in temperature, or the corresponding temperature difference ($\Delta t^{\circ}\text{C}$), versus time of the mixed solutions S/B_m, S/K, and P/B_b at different volume ratios of the stock solutions. The calorimetric curves of these tests are shown in Figures 2, 3, and 4. The curves demonstrate that the heat effect of mixing of all of the solutions is always negative, but of a small magnitude. The plot of temperature difference versus time passes through a minimum, which corresponds to a maximum of its absolute value. The maximum absolute value of the

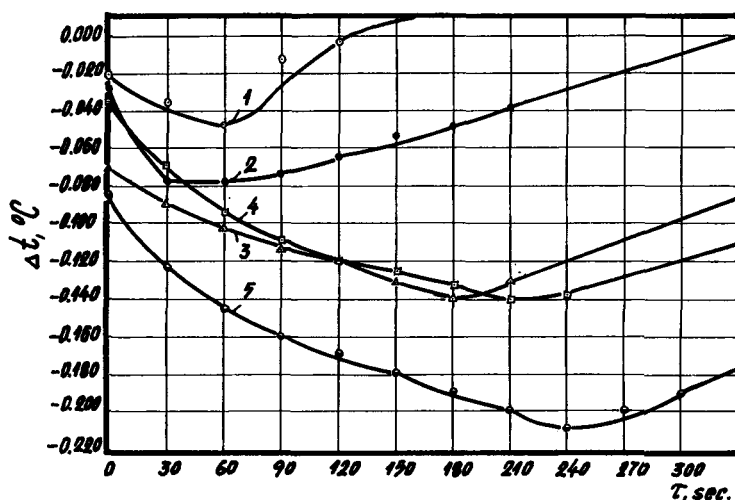


Fig. 2. Relationship between temperature difference ($\Delta t^{\circ}\text{C}$) and time of equilibration following mixing of the solutions SKN-26 and Balresin in varying volume ratios: (1) 9:1; (2) 8:2; (3) 7:3; (4) 6:4; (5) 5:5.

TABLE I
 Characteristics of the Stock and Mixed Solutions

Stock solution	Polymer	Solvent	Concentration, %	Mixed solution	
				Composition	Volume ratio
S	SKN-26	methyl ethyl ketone	15	S/B _m	from 9:1 to 5:5
P	Perbunan C 210	benzene	15	S/K	from 9:1 to 5:5
B _m	Balresin	methyl ethyl ketone	15	P/B _b	from 9:1 to 1:9
B _b	Balresin	benzene	15		
K	Kofenal 220	methyl ethyl ketone	15		

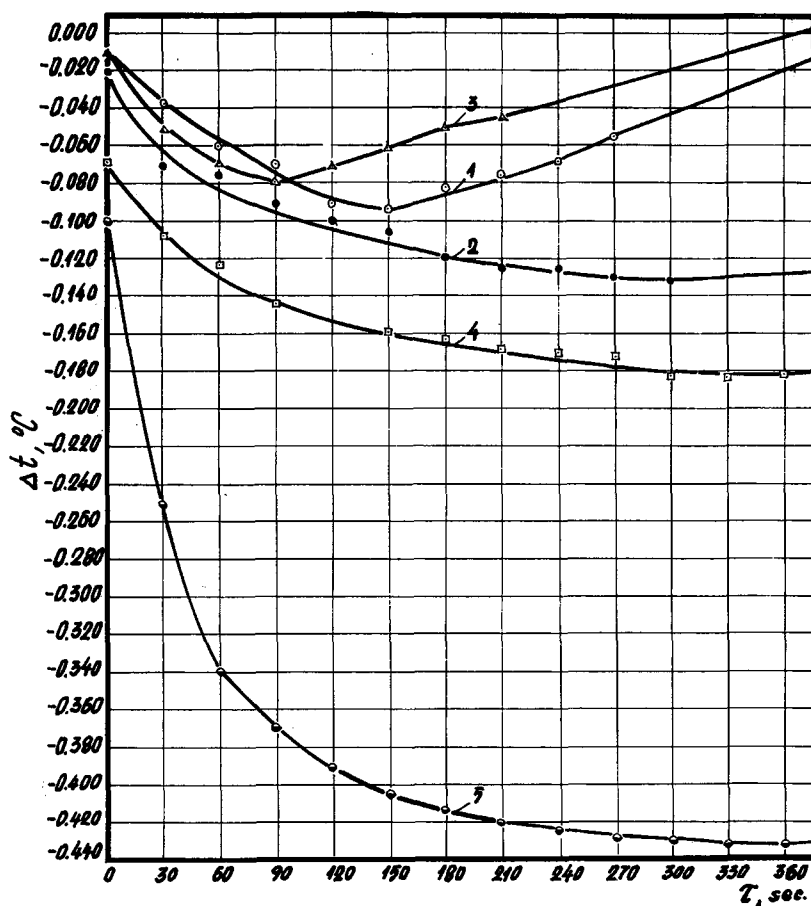


Fig. 3. Relationship between temperature difference (Δt , °C) and time of equilibration following mixing of solutions of SKN-26 and Kofenal 220 in varying volume ratios: (1) 9:1; (2) 8:2; (3) 7:3; (4) 6:4; (5) 5:5.

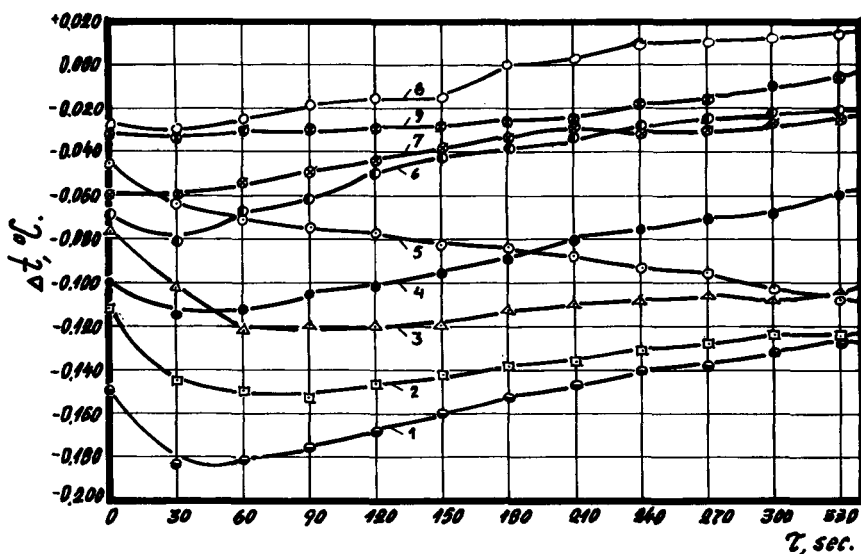


Fig. 4. Relationship between temperature difference (Δt , °C) and time of equilibration following mixing of solutions of Perbunan C 210 and Balresin in varying volume ratios: (1) 5:5; (2) 6:4; (3) 7:3; (4) 8:2; (5) 9:1; (6) 4:6; (7) 3:7; (8) 2:8; (9) 1:9.

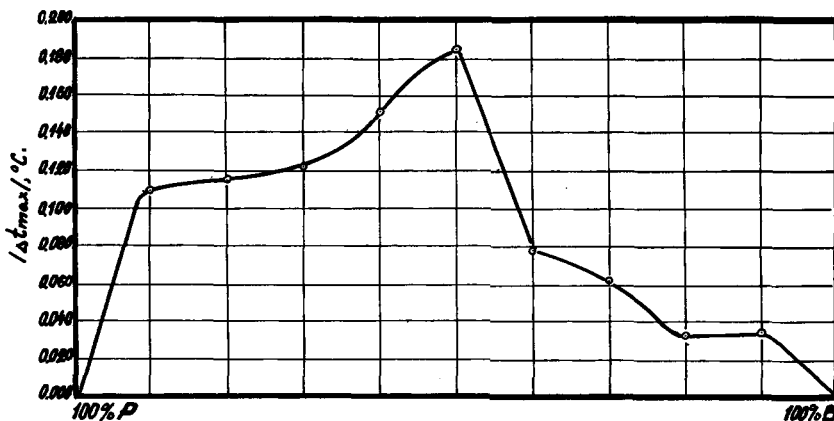


Fig. 5. Effect of volume ratio on the absolute value of Δt_{\max} in mixing solutions of Perbunan C 210 and Balresin.

temperature difference (Δt_{\max}) depends on the volume ratio and the type of stock solution.

Figure 5 illustrates the relationship between Δt_{\max} for the solution P/B_b and the volume ratio of the stock solutions. With the data taken from Figure 5 it can be established that the mixed solutions in which the rubber component predominates have a higher Δt_{\max} . The highest Δt_{\max} belongs to the solution obtained by mixing equimolar quantities of the stock solutions.

By comparing the curves in Figure 2 with those in Figure 3, it can be seen that the mixed solutions of the S/K type are characterized by higher Δt values than those of the S/B type. This is probably due to the more polar nature of Kofenal 220 as compared with Balresin.

The appearance of a slight negative heat effect and abrupt changes in Δt following the mixing of all solutions investigated in the present study give ground to the conclusion that a compatibility exists between SKN-26 and Balresin and Kofenal 220 and between Perbunan C 210 and Kofenal 220 over a wide range of ratios. No phase separation after mixing the stock solutions has been observed in any experiment. The conclusion of the compatibility has been confirmed by tests carried out on the optical properties of films obtained from all of the mixed solutions. All films cast from the mixtures in solution were transparent.

The ratio of the stock solutions can influence the magnitude of the heat effect, but does not affect the compatibility.

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Received April 27, 1971

Revised February 9, 1972