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INFLUENCE OF THE PROCESSING PARAMETERS ON THE STRENGTH CHARACTERISTICS OF THE UP/SBR POLYMER COMPOSITES

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ABSTRACT

The paper presents a study on the effect of processing parameters on the structure and the strength characteristics of multicomponent polymer systems based on unsaturated polyesters and elastomeric modifier. Relevant results obtained from scanning electron microscopy show a heterogeneous multiphase structure where the polyester resin forms the matrix and the elastomer – disperse phase. Both the size and distribution of the second phase particles depend on the processing parameters (rotor speed and mixing time). The influence of the investigated parameters on the strength when the polymer system is subjected to bending, impact and compressive stress loading was studied. It is shown that at low or high mixing rate and mixing time the strength characteristics of the polymer system are lower than the same for the unsaturated polyester resin, perhaps because of the non homogeneity or non sufficient particles size.

Optimal processing parameters considering highest strength characteristics of the polymer composite were determined.

Keywords: polymer composites, structure, processing parameters, strength characteristics, toughening.

INTRODUCTION

The modification of the thermosetting polymers by adding other polymer products, e.g. thermoplastics or elastomers, is a recognized method for compensating disadvantages such as high volume shrinkage in the course of hardening or brittleness and insufficient impact-resistance, as well as for developing new polymer composite materials [1, 2]. In most cases of modification the polymer modifier is of limited compatibility or it is incompatible with the basic polymer, which results in phase separation. When a chemical curing process runs along with a phase separation process, a polymeric composites structure depends to a great extent on the kinetic features and the speed ratio of the two processes. As a rule, phase separation processes precede chemical curing processes. Because of cross chemical bonds the former are not complete and disperse phase particles of different shape and size are formed [3,4]. The morphology of the polymer systems is a subject of a number of researches – it has been confirmed that the strengthening effect of the modifier is related to both its chemical nature and the morphological characteristics of the system. [5]. In view of the above mentioned, not only the colloid-chemical characteristics of the system (e.g. solubility parameters, phase surface tension, etc.), but also the processing conditions (the mixer type, duration of mixing, the rotation speed of the rotor or screw, the hardening conditions, etc.) have an influence on the structure of the polymer systems [7-9].

EXPERIMENTAL

Materials. Unsaturated polyester resin (UP) "Vinalkide 550 P" (Orgahim, Bulgaria) (acid number 25.7 mg KOH/g , M_n = 2130 determined by end groups titration) has been used as a main component of the system. The form offered by the manufacturer is a 66.8 % solution of the polyester in styrene. Butadienestyrene rubber **(SBR)** "Bulex 1500" ("Neftohim", Bulgaria) has been used as a polymer modifier (low-temperature copolymer of butadiene and styrene of an approximate styrene content of 43 %); used in the form of 20 % solution in styrene. The modifier content in the polymer system is from 0 to 1.00 vol.p. for viscosimetric measurements and from 0 to 0.22 vol. p. for strength characteristics tests.

Methods. The viscosimetric measurements have been taken by means of a rotational viscosimeter Rheotest 2.1(coaxial cylinders), at a speed of 0.2 - 1.3 10^3 s^{-1}, in a temperature range of 25 - 85°C. The shear stress [Pa] has been calculated as $\tau = M/2\pi lr^2$, and the shear rate γ [s^{-1}] as $\gamma = 2\omega R^2/R^2\text{-}r^2$, where: M is the torque moment, ω - the rotation speed, l – the length of the cylinder, R and r – respectively, the radii of the external and internal cylinder. The efficient viscosity η, [Pa.s] has been determined as $\eta = \tau / \gamma$. The initial Newtonian viscosity η_0 has been determined from the Y-axis segment of the $\eta = f(\lg \tau)$ dependence when $\tau \rightarrow 0$.

The phase structure of the polymer composites has been observed on a Philips 500 scanning electronic microscope by assessing the cross-section surface of the breaking in liquid nitrogen specimens..

By measuring the compressive strength, the bending strength and the impact -resistance the strength characteristics have been determined. The compressive strength σ_c, [Mpa], (BDS EN ISO 604:2004) was determined on a ZD 10/90 device at a motion speed of the plates - 0,2 mm/s and measurement accuracy of ±1%; bending strength σ_b, [MPa] (BDS EN ISO 178:2002) - determined on a "Schopper" dynamometer at a uniform speed of deformation 30 mm/min (span - 40 mm) and measurement accuracy of 1%; impact resistance σ_{ir} [J/m^2] (BDS EN ISO 179-2:2003) – determined according to Sharpi (pendulum power of 1.0 J, span of 40 mm), on standard unnotched specimens.

Specimens. The polymer composites have been produced by mixing together the main component and the polymer additive. To assess the impact of the mixing parameters on the structure and strength characteristics of the polymer systems, the specimens have been made under the following mixing conditions: rotation speed of the mixer rotor - 200, 700 and 1200 min^{-1}; duration of mixing - 5, 10, 15 and 20 min. The quantities of the polyester and the polymer additive have been mixed well by means of a high-rotational speed mixer. Cyclohexanonperoxide in the form of a 50 % solution in dioctylphtalat (activation disintegration energy 121.4 kJ mol^{-1}, content of the active oxygen - 9.1%) has been used as an initiator for the hardening process, and cobalt naphthenate has been used as an accelerator. The concentration of the initiator and accelerator is 2 % toward polyester's mass. The initiator and accelerator have been added consecutively to the mixture by well mixing for 5-10 s each. The specimens have been cast in polypropylene moulds of a size specified in the standard. They have been cured at room temperature for 24 h, and then thermally processed 2 h at a temperature 80°C.

The specimens have been broken in liquid nitrogen and their surface gilded for assessing their structure by SEM.

RESULTS AND DISCUSSIONS

Colloid-chemical characteristics of the polymer system and compatibility of the components. As it is well known, when two polymers are mixed together, polymer systems whose colloid-chemical characteristics are determined by the compatibility level of their components, occur [4]. For the system been studied the compatibility level has been assesses by two relatively simple methods: visual assessment of the system's transparency and the correlation between the viscosity dependences and the additive curve.

The visual assessment of the transparency level shows that when the resin and the polymer additive are mixed together, the mixture gets turbid, i.e. the system obtained is non-homogeneous. In addition, if the mixture is left for a longer period at rest, its components segregate, which demonstrates the incompatibility of the components as well. The compatibility of the components can also be assessed indirectly by the location of the concentration dependences of the initial viscosity against the additive curve of the two polymers. The comparison is based on the initial viscosity when $t \rightarrow 0$ [4].

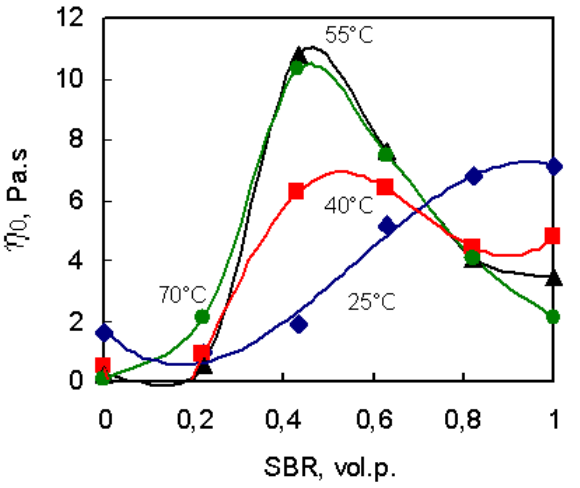

Fig. 1. Concentration dependences of h_0 for a UP/SBR polymer system in a temperature interval of 25-70°C.

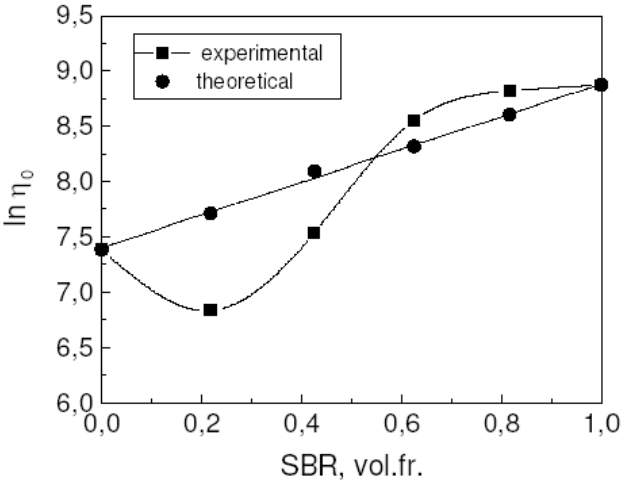

Fig. 2. Test assessment of the viscosity of the UP/SBR system according to the rule of logarithmic additivity.

The data obtained from the viscosimetric measurements (Fig.1) show that at a temperature of 25°C in the concentration interval studied, the curve determined by the values of the initial viscosity at different resin/additive concentration ratios is almost completely below the additive straight line. When temperature rises, the dependence changes – at 40°C only composites with very low or very high content of rubber remain under the additive line; at 55°C only the composites with low rubber content is below the additive line; whereas at 70°C the whole curve is above the additive line. The occurrence of concentration intervals where the viscosity is above the additive line for the two polymers is related to the change in the thermodynamic stability of the polymer systems, which is a result of the temperature influence on the processes of phase separation. With the polymer systems of a polymer-polymer-solvent type, which is the studied one, the occurrence or loss of homogeneity is a function of the intermolecular interactions and the free volume [4].

According to Utracki [10], every dependence describing the flow behaviour of the polymer systems combines three components: the concentration gradient, the orientation and the tension-deformation dependence, by taking into consideration the influence of the structure changes in the flow behaviour. The tests results show that for the mixtures of incompatible polymers, there are five different types of rheologic behaviour: mixtures with a positive deviation from the additivity rule, mixtures with a negative deviation from the additivity rule, mixtures corresponding to the logarithmic additivity rule, mixtures with a positive-negative deviation, and mixtures with a negative-positive deviation. The difference in the rheological behavior can be caused by structural changes, concentration gradients and orientation effects in the flow out, occurring under the influence of the stress, and depending on the stream structure. The rheologic qualities are influenced not only by the structural nonhomogeneity or concentration gradients but also by the presence of an interphase layer as a result of phase separation at the boundary between the domains of disperse phase and the matrix. Since the interphase layer has a particular thickness and composition, in some cases it is considered as a third phase with specific rheologic characteristics.

The presence of a polymer additive, which has a considerably higher viscosity than that of the resin (the viscosity relationship at 25°C is $\lambda = 4.7$), results in increasing the viscosity of the system. The composite shows a negative-positive deviation from the additivity (Fig. 2), and the analytical dependence describing the test curve with the highest probability are expressed in the following way:

- for contents of SBR $\phi = 0 - 0.55$ vol. parts: $\ln \eta_0 = 7.347 - 3.807\phi + 9.285\phi^2$
- for contents of $\phi = 0.55 - 1.00$ vol. parts: $\ln \eta_0 = 3.908 + 11.28\phi - 6.334\phi^2$

Phase Structure of the Polymer Composites

The data from the SEM tests indicate structural nonhomogeneity of the composities obtained (Fig. 3), which confirms the conclusions drawn on the basis of viscosimetry. The polymer system is a two-phase system where the UP forms the disperse environment (continuous phase) in which the polymer additive is distributed in the form of domains of different sizes (disperse phase). The particles of the disperse phase are also nonhomogeneous – inside them there are segments, probably of UP, involved in the hardening process as a result of the incomplete phase separation.

Such a structure of a phase-in-phase type has been observed also in other heterogeneous polymer systems, containing rubber. Sperling [11] defines them as semi-interpenetrating networks.

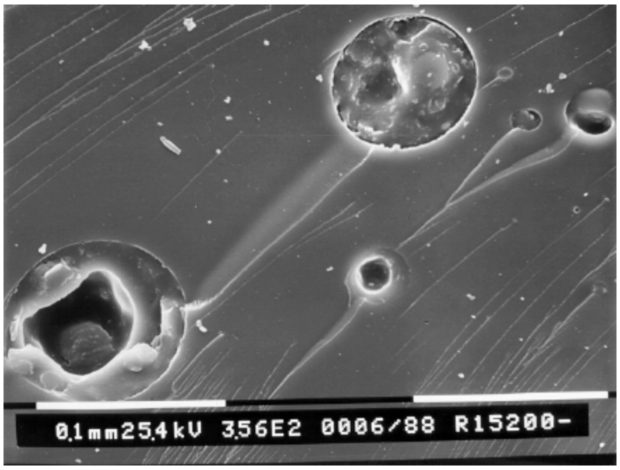

Fig. 3. SEM-Microphotographies of a UP/SBR polymer system of 10 mass % SBR: time -15 min, speed- 200 min^{-1}.

Influence of the Mixing Parameters on the Structure and Strength Characteristics of the Composites. The size and distribution of the particles in the second phase are directly dependent on the mixing conditions. When increasing the rotational speed of the mixer from 200 min^{-1} to 1200 min^{-1} for a define period of time, the number of the disperse phase particles increases whereas their size decreases (Figs. 3 and 4). A similar tendency is observed when the duration of the process is prolonged from 5 to 15 min. at a constant speed of mixing. In view of the above mentioned, one of the following two parameters could be used – rotational speed or mixing time, in order to regulate the distribution of the particles of the second polymer, and respectively the qualities of the polymer system as a whole, since it is known that the size of the disperse phase particles determines, to a great extent, the strength characteristics of the composite.

Bending strength. By studying the dependence of the strength characteristics on the mixing parameters, it can be seen that when the speed and the duration of mixing are increased, the bending strength passes, in general, through the maximum where the highest values of the characteristic are at a speed of 700 min^{-1} and duration of 15 min (Fig. 5). At lower and higher speeds and mixing time the bending strength decreases. .

Compressive strength. Unlike the bending strength, the values of the compressive strength show a relatively small change when increasing the speed and the mixing

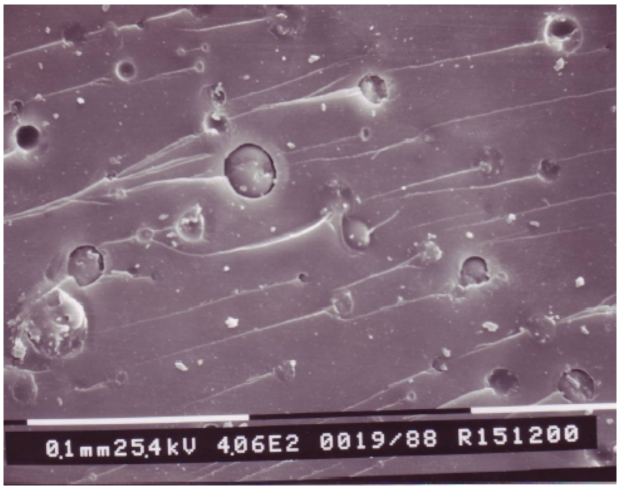

Fig. 4. SEM- Microphotographies UP/SBR polymer system of 10 mass % SBR: time -15 min, speed 1200 min^{-1}.

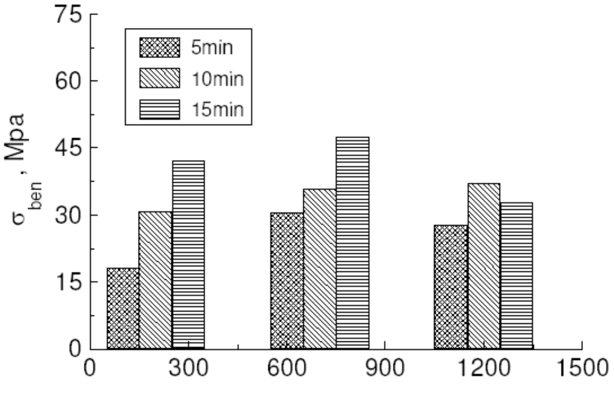

Fig. 5. Influence of the mixing parameters on the bending strength of a UP/SBR polymer system.

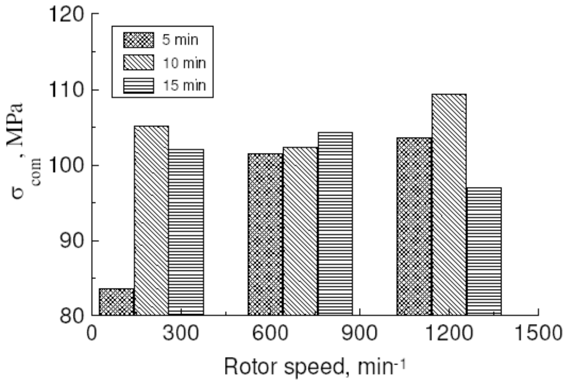

Fig. 6. Influence of the mixing parameters on the compressive strength of a UP/SBR system.

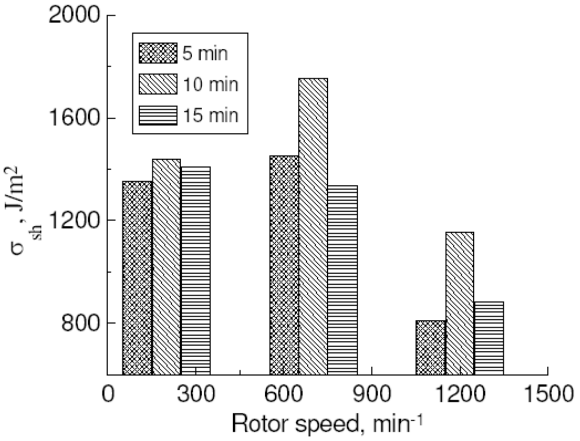

Fig. 7. Influence of the mixing parameters on the shock-resistance of a UP/SBR polymer system.

time (Fig. 6). The value remains relatively high at a speed of 700 min^{-1} and mixing time of 10 min.

Impact strength. The highest values of the impact resistance are observed at a speed of 700 min^{-1} and mixing time of 10 min (Fig.7). The lower values at a low speed are probably caused by the insufficient degree of homogeneity of the components. As a result, during the process of hardening a phase with non-uniformly distributed rough particles which increase the defectiveness of the matrix is formed. A considerably low impact resistance is observed at a mixing speed of 1200 min^{-1}. The studies of systems strengthened by thermosets and elastomers show also that an actual strengthening effect can be observed with particles of 50 mm size [7]. Since for the given mixing mode the size of the particles is reduced, at 1200 min^{-1} the strengthening effect of the polymer additive decreases as well.

The concentration dependence of the impact resistance at a speed of 700 min^{-1} and mixing time of 10 min, expressed by the degree of toughening (Table 1), indicates a maximum strengthening effect of the additive for contents of 0.05 and 0.32 vol. p. The degree of toughening is determined as a relationship between the inpact resistance values of the polymer composites σ_{SBR} and the pure resin: σ_{shUP}: $N_{yc} = (\sigma_{SBR}/\sigma_{UP}).100$, %.

A similar influence of the strengthening additive in the area of the low concentrations has been observed when testing rubber-strengthened epoxy resins, too [12]. The fact that a real modifying effect is observed in the areas of the low content of additive confirms the theoretical views on the strengthening effect of small amounts of a polymer modifier on the thermosets [13]. The mechanisms of the strengthening effect of the elastomers when there are different contents have been established different. According to Lipatov's theory, the strengthening effect in the low concentration areas can be explained by the specific structure formed by the polymer additive in the polyester matrix, i.e. in terms of the colloid-chemical characteristics of the system. According to him this effect is analogy with the phase-separation processes whose nature resembles that of the dendritic liquation when metal alloys are crystallized. As a result of these processes, the polymer matrix and the modifier form a frame structure of a coagulation or condensation type, which leads to the strengthening effect [3]. May be the "craze" theory can be applied to higher concentrations. It is based on the structural changes in the materials when an external force is applied [11].

However, the actual strengthening effect is probably caused by the synergic action of the different mechanisms, which in turn is determined by the structural characteristics of the system [14].

CONCLUSIONS

The polymer composites tested can be described as multi-phase heterogeneous disperse systems. This heterogeneity results from the incomplete phase-separation processes running simultaneously with the chemical curing processes. The phase-separation processes are determined by the incompatibility of the components in the concentration interval studied, which is confirmed by the viscosimetric tests.

Table 1. Values for the shock-resistance and the degree of toughening for a UP/SBR system.

SBR, w.%	Shock strength, kJ.m^{-2}	Toughening, %
0	1.6	100
0.01	1.8	116
0.033	1.7	110
0.055	2.6	166
0.072	1.5	113
0.11	1.7	110
0.165	2.2	138
0.22	2.0	129
0.28	1.9	125
0.32	2.2	180

The tests of the hardened polymer systems show a non-homogeneous phase structure which is typical for the mixtures of incompatible polymers, where the unsaturated polyester forms the disperse environment and the elastomer – the disperse phase. The disperse phase particles are also non-homogeneous probably because of the involvement of part of the disperse environment in the phase separation – the so called *phase-in-phase* structure.

The mixing parameters influence the distribution and the size of the disperse phase particles, and respectively the physical and mechanical characteristics of the polymer system. The optimal conditions for mixing the components in order to obtain maximum physical and mechanical characteristics for the system studied are: rotor speed of 700 min^{-1} and mixing time of 10 min.

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