ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 9, No. 3. 2003

The Modification of Rheological Behaviour of Solvent – Based Adhesive by Disperse Filling

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Received 15 October 2002; accepted 31 January 2003

The possibility to modify rheological behaviour of solvent-based polychloroprene adhesives by various amounts of dispersed secondary polypropylene particles has been investigated. It was shown that obtained compositions in investigated shear flow conditions shows non-Newtonian behaviour typical for concentrated polymer solutions. The pseudoplasticity of solutions was evaluated according to means of shear thinning index. It was found that increase of both filler and solution solid content increase compositions pseudoplastisty. Independently on solution solid content the increase of filler content leads to decrease of solution viscosity, also.

Concentration-time superposition was applied to identify the role of filler content and solution concentration on relaxation properties of polychloroprene adhesive. The increase of filler content increase the relaxation function and this effect is higher the higher solution concentration. On the other hand, construction of filler content – solution concentration - invariant curve showed that, decrease of solution concentration leads to the increase of extensity of master curve and decrease of intensity of relaxation processes.

Keywords: solution, rheology, viscosity, polychloroprene adhesive, disperse filler, aged polypropylene.

INTRODUCTION

The adhesion to thermoplastics has been gaining increasing importance academically as well as industrially in the past several years. However, the surface of thermoplastics, such as polyethylene, polypropylene is inherently incompatible with typically higher surface energy structural adhesives. This is major cause of their lack of good adhesion properties [1]. Several techniques are available to modify surface properties that in some way lead to improved adhesion. As example can be sulfanation, plasma and corona discharge, flame treatment and acid etching [2]. However, this kind of surface treatment is expensive and time consuming. Another, the cheaper alternative to modify mechanism of interaction is special additives for adhesive compositions. Due to them structure of film forming polymer is changed and in the same way bond strength between substrate and adhesive can be increased.

In the last several years the investigation toward increase of the adhesion between polychloroprene adhesive and polypropylene substrate was made. It was found that after ageing dispersed polypropylene improves strength of both adhesive and especially of adhesive moulded joints between polypropylene and leather. During oxidation the reorganisation of polymer structure occurs due to creation of high surface energy functional groups, such as hydroxy, oxy, carboxyl, aldehyde, ketone and others [3, 4]. Such groups efficiently promote adhesion by increasing wettability of the surface and provide the necessary functionalities to use this waste as a filler in adhesive compositions [5].

The obtained solvent-based adhesive compositions are multi – component and multi - phase systems. The complex set of properties, which they display, rather own to the peculiarities of their structure. This makes it difficult to draw any general conclusions on their behaviour, and compare with those, studied for homogenous polymers [6]. For all the compositions exist a general problem of the effect of their constituents on the viscosity, elasticity, and relaxation properties of the material.

The rheological behaviour of disperse filled compositions has received increasing attention in the recent years [7, 8]. This is because rheological behaviour is a problem in industrial application of concentrated suspensions, dispersions, latex, etc. which exhibit very strong rheological effects, usually related to the microstructure of composition [9]. The mechanical and rheological properties of polymer composition are of interest attributed not only to the various technological issues of adhesion, blending, and lubrication, but they are also interesting from a scientific perspective as an prognosis of the behaviour in the wide range of external forces [10].

The main goal of this investigation was to show ability to modify polychloroprene adhesive behaviour under shear conditions by disperse filling and find out effects related to both filler and solution solid content.

EXPERIMENTAL

The material under investigation was solvent-based polychloroprene adhesive compositions filled with different amounts of after ageing dispersed polypropylene particles. The adhesive solutions in organic solvents were based on poly-2-chlorobutadiene (mercaptane modified) rubber Baypren 330 (producer is Bayer AG, Germany). Before dissolution required amount of rubber was premasticized by milling at ambient temperature for 10 min. The solid content in adhesive solutions was 15, 20 and 25 percent.

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Dispersed after thermo ageing at $T = 150$ °C temperature for 200 hours isotactic polypropylene (aPP) (producer is UFA ORGSYNTHESIS, Russia) was used as filler. The specific surface area of polydispersed particles was $S_{sp} = 200$ m^2/kg. The amounts of 0 – 60 parts per hundred of rubber (phr) were added to polychloroprene adhesive solution. In order to maintain constant composition concentration, additional amount of solvent after filling was added. Homogenisation of compositions was performed at high rotational speed ($\omega = 2800$ s^{-1}) for 5 min.

Rheological measurements were carried out in rotational viscometer RHEOTEST 2.1 at the ambient temperature ($T = 20 \pm 3$ °C), which was controlled with the rheometer equipped fluid bath. The flow cell consisted of inner cylinder, rotating at shear rate $\gamma = 0 - 10^3$ s^{-1}, while the outer concentric cylinder was held stationary. The ratio between external and inner cylinders radius was 1.02. After sample loading, the mixture was presheared for 1 min at an intermediate shear rate to overcome any initial wall effect, occurring due to plug flow conditions occurring during insertion of the inner cylinder in the outer one.

RESULTS AND DISCUSSIONS

The effect of filling for polychloroprene adhesive compositions containing various solid content on their rheological behaviour under various shear rates are presented in Fig. 1. For more detail representation of the decrease of viscosity with increasing velocity gradient in shear, shear thinning index (STI) was calculated. In this case, STI represents the ratio of viscosities for the each curve, presented in Fig. 1, at shear rates $\dot{\gamma} = 1.35$ s^{-1} and $\dot{\gamma} = 48.96$ s^{-1}. Theoretically, STI is a quantitative measure of the pseudoplasticity. If STI = 1, the solution behaves as a Newtonian fluid, and for STI > 1 pseudoplastic behaviour of investigated solution is characteristic [11]. According to in Fig. 2 presented variations of STI values in dependence on filler and solid content in adhesive composition, it can be stated, that all of them show pseudoplasticity, because all of STI values are higher than 1. Thereby, the linear relationship between STI values and filler content is obtained, but the intensity and character of this effect depends on composition solid content. It seems, that the effect of filling on solutions pseudoplasticity was negligible for solutions in which solid content was 20 and 25 %. The STI values for compositions with 25 % solid content show slightly decrease when filler content increases. The STI decreases only in 13 % when results of unfilled and filled by 60 phr of aPP compositions were compared. The filling practically does not influence on the shear thinning of solution containing 20 % of solid phase: the trendline obtained after data approximation is parallel to abscise axis. In that time the plot obtained for adhesive compositions, in which solid content was 15 %, shows that the increase of filler content significantly alerts the flow field and increases solution pseudoplastisity. The addition of 60 phr of aPP particles, more than two - fold increases values of STI. These results suggest that the lower solution solid content, the higher polypropylene particles effect on the adhesive rheological behaviour is reached.

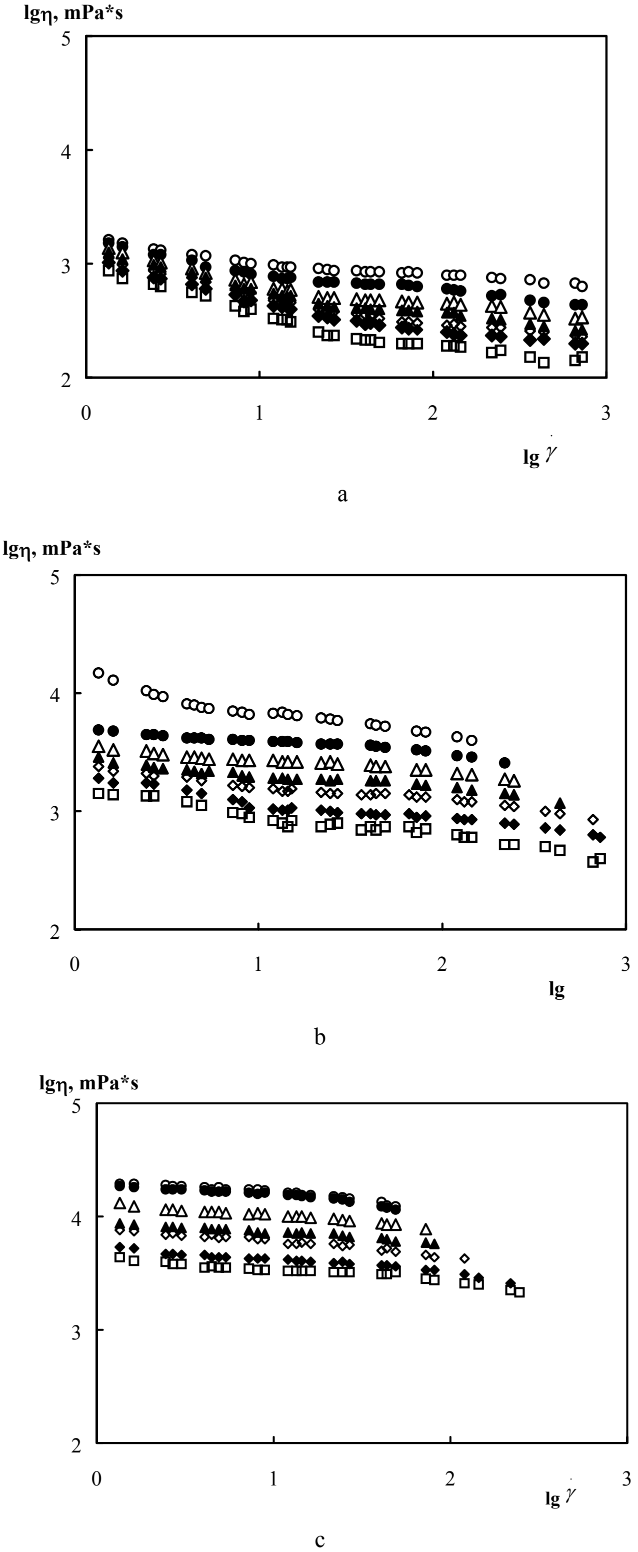

Fig 1. Variation of viscosity η, mPa·s as a function of the shear rate $\dot{\gamma}$, s^{-1} in dependence on filler content φ, phr (○ – 0, ● – 10, Δ – 20, ▲ – 30, ◇ – 40, ◆ – 50, □ – 60) for various solid content rates C, % (a – 15, b – 20, c – 25) in PCP adhesive compositions

From Fig. 1 also it can be stated that, independently on the solid content rate, the increase of filler content leads to the decrease of adhesive viscosity. In order to evaluate efficiency rate of the filling the specific viscosity η_{sp}, expressed as

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0}, \qquad (1)$$

was calculated [11]. Where η_0 and η are the viscosities of unfilled and filled PCP solution, respectively, at the shear rate $\dot{\gamma} = 48.96\ \mathrm{s}^{-1}$.

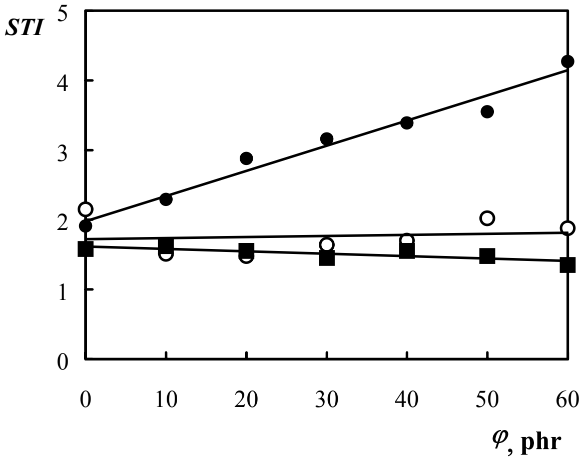

Fig. 2. Variation of STI as a function of the filling rate φ, phr, for PCP adhesive compositions containing various solid content rates *C*, % (● – 15,○ – 20, ■ – 25)

The results of this evaluations are illustrated in Fig. 3. The obtained curves slope and negative values of specific viscosity η_{sp} show, that the increase of filler content leads to the monotonous decrease of solution viscosity. It seems that at the high filling rate ($\varphi = 60$ phr), independently on the composition solid content, the solution viscosity decreases more than 70 %, compare to those of unfilled.

The above observed results can be explained by several suggestions. At first, the decrease of viscosity for unfilled adhesives shows typical flow behaviour for non - Newtonian system. The spatial structure of polychloroprene macromolecules are related to the shape of macromolecules, their intra- and intermolecular interactions, and formation various structural units: enlanglements (nodes, junctions). The decrease of viscosity under shear can be related to the destroying some of these linkages [13]. As the filler is added, due to its capability to interact with polymer, the hydrodynamic effects are supplemented with specific surface phenomena, which may be treated as the formation of a transient layer between the matrix and the filler. Besides, the interaction between filler particles may result on the formation of a structural skeleton in the liquid phase, which may be broken down under the influence of external forces [14].

For the practical suggestions, these data show that the presence of the structural skeleton of the filler or of its fragments impeded the manifestation of the viscoelasticity of the dispersion medium and requires the decrease of the stresses necessary for the development of deformations that were produced in a pure polymer [11]. Besides, the low viscosity adhesives show improved ability in the substrate surface wetting and the microrheological processes in the interface proceed more fully. Meanwhile, the decrease of the viscosity can lead to the reducing of the amount of organic solvents in adhesive composition without decrease of film forming polymer amount and decrease of volatile solvents amount emission in air, also [4, 12].

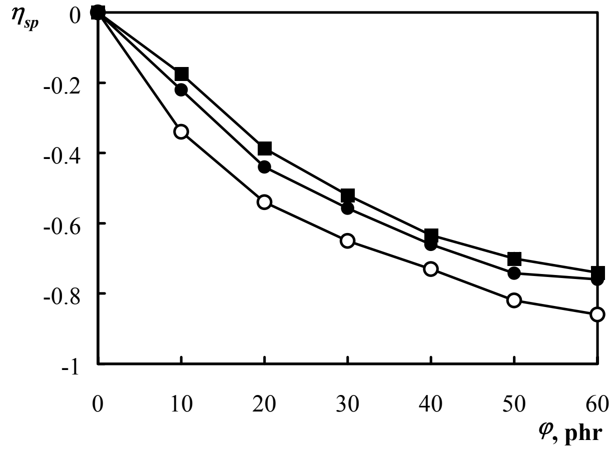

Fig. 3. The effect of filling rate on specific viscosity η_{sp} measured at shear rate $\dot{\gamma} = 48.96\ \mathrm{s}^{-1}$ for PCP adhesive (marked as in Fig. 2)

As the viscosity is a decreasing function of filler content, the concentration-time superposition principle analogy of viscoelasticity, which describes the dependence of viscosity on the filler or main film-forming polymer content as follows, can be used for prognosis of adhesive solution behaviour in a wide shear rate range. The empirical approach to the construction of the concentration-time curves for the generalization viscoelestic properties of polymer systems is based on the observation of the temperature superposition, known as Williams-Landel-Ferry relation [15]. The method of constructing a master curve for the concentration-invariant description of viscosity enables one to determine the value of viscosity η at various shear rates $\dot{\gamma}$ for various filler content φ if the filler content dependence on the solution viscosity at any filler content is known [15]. According to the obtained experimental results (Fig. 1) it can be stated, that the change of the aPP particles amount from φ_1 to φ_2 at the same solution solid content does not affect the functional dependence of viscosity η on the shear rate $\dot{\gamma}$. So, the viscosity curve at each filler content φ in the lg(η) versus lg($\dot{\gamma}$) plot, was horizontally shifted by a "shift factor" lg a_φ with respect to the viscosity curve, which represents behaviour of adhesive composition, containing 10 phr of aPP particles. In this way there are obtained the master curves of lg(η) *vs* lg($\dot{\gamma}\, a_\varphi$) reduced to the reference filler content of $\varphi = 10$ phr. The results of reduction procedure, during which the filler content dependence of the shift factor lg a_φ, and the a filler content-invariant master curve was constructed, are presented in Fig. 4.

By the physical meaning, shift factor lg a_φ is the ratio of maximum relaxation times at different filler content to the maximum relaxation time of the reference filler content of $\varphi_0 = 10$ phr, to which reduction is made. The function lg $a_\varphi = f(\varphi)$ characterizes the influence of the filler content on maximum relaxation times. From the comparison of the location of obtained data in respect to each other (Fig. 4), it can be suggested that the increase of filler content leads

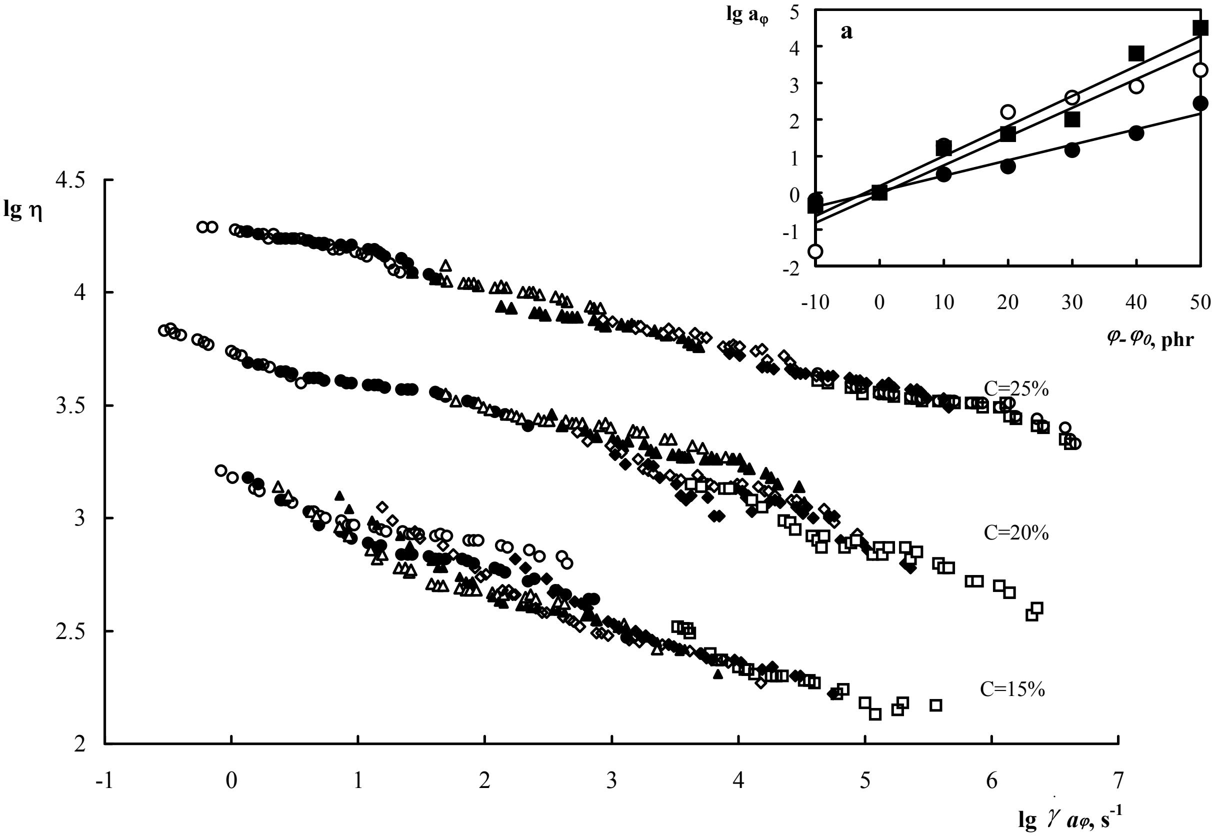

Fig. 4. Master curves of the viscosity as a function of filler content in adhesive composition and filler content-time dependence shift factor a_φ for solutions with different solid content C, % (● – 15, ○ – 20, □ – 25)

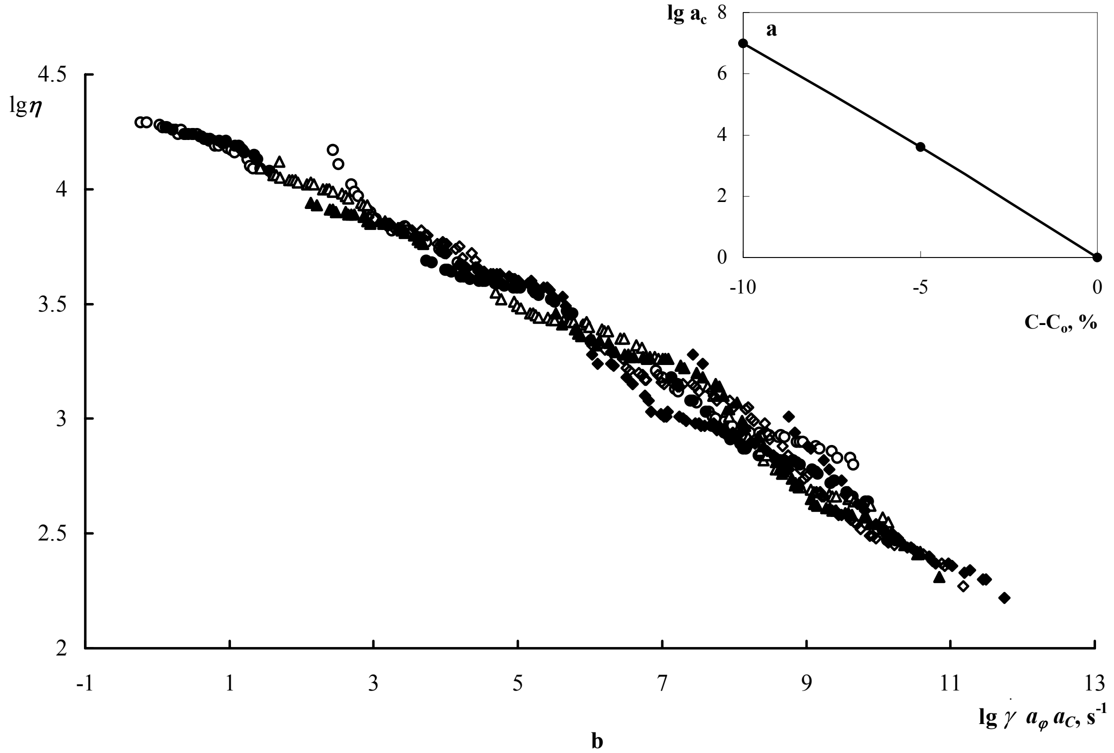

Fig. 5. Master curve obtained according to the experimental results for solutions with different solid content C, %, and filling rate φ, phr, and concentration-time dependence of shift factor a_C

to the increase of relaxation function. This effect is higher the higher adhesive composition solid content. For all compositions the experimental means of the dimensionless shift factor $\lg a_\varphi$ shows linear relationship in coordinates $\lg a_\varphi - (\varphi - \varphi_0)$ with high correlation of obtained data according to the relation

$$lg\, a_c = a(\varphi - \varphi_0) + b \ . \tag{2}$$

Table 1 also presents the values of both empirical coefficients *a* and *b* determined by the method of least squares. The clear tendency of the values increase by the increase of composition solid content were found.

Table 1. The parameters of Eq. (1)

Solution concentration C, %	Coefficients of Eq (1)		Correlation coefficient R^2
	a	b	
15	0.0432	–0.0193	0.95
20	0.0663	0.1893	0.95
25	0.0815	0.5161	0.95

The experimental points dissipation obtained in the constructed master curves shows that all of them, independently on solution solid content *C*, lays well in the dependence of transformed shear rate $\lg(\dot{\gamma}\, a_\varphi)$.

As the obtained filler content-invariant curves were similar in form, the above presented master curve constructing method was used for the construction of the filler content – composition solid content – invariant curve. All curves presented in Fig. 4 were superimposed by shifting them horizontally along the axis $\lg(\dot{\gamma}\, a_\varphi)$ by an amount equal to the concentration shift factor $\lg a_C$. The reference adhesive solution concentration was found of $C_0 = 25\%$, filler content $\varphi_0 = 0$ phr. The master curve of the viscosity as a function of both aPP particles content and the adhesive solid content are presented in Fig. 5. There variation of shift factor a_c is presented, also. It seems that decrease of solid content leads to the increase of shift factor values. Besides, linearity between shift factor values and reduced concentration (Fig. 5), which can be expressed according empirical relation $\lg a_C = -0.7(C - C_0) + 0.0333$ ($R^2 = 0.9997$) was determined. The obtained data also show that the increase of shift factor a_C values leads to the increase of extensity of the master curve (Fig. 5) and characterizes the decrease of intensity of relaxation processes.

CONCLUSIONS

Modification of rheological behaviour of polychloroprene adhesive containing different solid content with various amounts of polydisperse aged polypropylene particles has been investigated. The filled and unfilled adhesive compositions show pseudoplastic behaviour, i.e. decrease of viscosity at steady shear flow conditions. The higher adhesive solid content the higher pseupoplasticity for compositions with increase of filler content is achieved. Besides, the increase of filler content leads on the decrease of the adhesive compositions viscosity, also.

The concentration-time superposition was applied for construction master curves for evaluation relaxation properties and for prognosis of the adhesive compositions behaviour under various shear rates. The increase of filler content leads to the increase of relaxation function and this effect is higher the higher adhesive solid content. On the other hand, the decrease of the solution viscosity, found as a result of minimization of solution solid content, influences on decrease of relaxation processes intensity.

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Paper presented at the XI International Baltic Conference
“Materials Engineering & Tribology - 2002”,
November 14 - 15, 2002, Kaunas, Lithuania