Rheology of plasticized polymer solutions

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Abstract
This paper is about rheological properties of plasticized polymer solutions with different concentration of plasticizer. It was established that the investigated polymer solutions were three-dimensionally structured systems which were shear thickened at low shear rates and maintained the thixotropic structural state under high shear rates. However, addition of different amount of plasticizer had an ambiguous influence on rheology of solutions and led to formation of transient polymer network with a complicated character of structuration because of the features of interaction in the polymer - plasticizer system. It was found that the plasticization results in changing of EC molecules conformation and simultaneous breaking of the polymer continuity due to DBP adsorption on EC macromolecule. Herewith, the formation of smaller crystallites took place. Besides, the investigated solutions showed causal link between structural states.

Keywords: rheology, polymer, rheopexy, pseudoplasticity, thixotropy
Kulcsszavak: reológia, polimer, reopexia, pszeudoképlékenység, tixotrópia

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1. Introduction

Rheological behavior of concentrated suspensions is an important area of research because it provides rich information, concerning flow and storage of relevant materials under operation conditions. There are many publications focusing on rheology of polymer concentrated suspensions filled with metal oxide powders of various particle diameters. The rheological properties depend on the solid phase concentration [1-3], particle size[2, 4-6], concentration and molecular weight of polymer [1-3, 5-7] and also interaction between particles, solvent and polymer molecules [2, 5, 9]. Because of rapid development of microelectronics, the suspensions based on nanopowders represent the most promising objects for rheological investigations. Herewith, nanosized particles allow obtaining *green* ceramic layers with thickness of 700 to 800 nm and surface parameter Ra commensurable with size of nanoparticle [10].

It is known that screen printing pastes based on micron powders are generally required to be shear thinning, thixotropic over definite time scale and shear rate, stable for screen/shelf-life and low solvent evaporation [11-13]. Therefore, terpineol [14-21] and its derivatives [17, 20, 22-25, 26-29] are used as a solvent, ethylcellulose as an organic binder [14, 15-21, 30-42] because of their ability to form thixotropic systems with suspensions of particles of various origination [43]. However, there is almost no information about rheology of ethyl cellulose solutions in terpineol with the exception of [44]. In turn, it is the main factor that reflects structural features of polymer and determines degree of interaction with surface of solid particles.

In this work, the dependence of the rheological properties of ethyl cellulose (EC) solutions in terpineol (Terp) on plasticizer dibutyl phthalate (DBP) content has been studied to improve elastic properties of polymer, pastes and films based on them [45-53]. In general, the plasticization leads to decreasing the glass transition temperature, fluidity and improving the mechanical properties due to reduced interaction between macromolecules and mobility of enhanced segments [54-58]. Normally, plasticization implies great change of structural-mechanical properties [55, 58, 59] due to interaction features in polymer - plasticizer system. The polymer macromolecule conformation and flow character of the appropriate solution are changing. Plasticizer influence, however, is not limited by rearrangement inside the EC molecule. EC is a rigid-chain polymer peculiar to polymorphism [60-62] – it forms individual crystallites in the form of packed antiparallel separate segments of macromolecule [63-65]. According to that, the DBP concentration should affect the polymer crystallization rate due to molecule re-conformation.

Therefore, this paper is about the features of viscosity and rheological behavior in the EC-DBF polymer systems depending on DBP concentration.

2. Materials and methods

Investigated solutions were prepared under heating and permanent stirring conditions. Terpineol was used as a solvent (mixture of α- and β-terpineol isomers, Merck GmbH) forethyl cellulose (10 cP, Merck GmbH) as an organic binder and dibutyl phthalate (Merck GmbH) as a plasticizer.

The rheological tests of the solutions has been carried out using rotary rheometer Rheotest RN4.1, Medingen at shear stresses from 1 to 1000 Pa and gap between coaxial cylinders of 1.48 mm. All measurements were carried out at 20±0.5°C. Herewith, the variable was DBP concentration in the solutions (changing from 0 to 40 m%).

Thixotropy and rheopexy degrees were determined from the hysteresis loop areas between up- and down-curves. In turn, the hysteresis loop area has a dimensionality of energy, correlated to sheared volume and determines the value of energy consumed for disrupting of thixotropic (rheopexic) structure [66].

A criterion of equilibrium degree of structure destruction (EDSD) for effective viscosity is determined as follows:

$$\mathrm{EDSD} = \frac{\eta_{\mathrm{Max}}-\eta_{\tau}}{\eta_{\mathrm{Max}}-\eta_{\infty}},$$

where η_τ– is the effective viscosity at given shear stress; η_{Max}– is a maximal viscosity corresponding to nonvolatile initial structure; – η_∞ is the less viscosity, corresponding to breaking point [67]. When EDSD < 1 the recovery processes prevail destruction processes and vice-versa when EDSD > 1.

Dilatancy degree D is characterized by the strength of sheared initial structure [68] and determined as:

$$\mathrm{D} = \frac{\eta_{\mathrm{Max}}-\eta_{\tau}}{\eta_{\tau}},$$

where η_{Max}– is the maximal viscosity corresponding to nonvolatile initial structure; η_τ – is the effective viscosity at given shear stress.

3. Results and discussion

3.1 Rheology of initial polymer solution EC+Terp

Fig. 1 shows viscosity profiles of EC+Terp solution PP1. Significant difference between up-curve and down-curve suggests PP1 as structurized polymer system with complicated flow due to the presence of two hysteresis loops. Accorging to the hysteresis loop in *Fig. 1* a rheopexic structure is undegone destruction at shear stresses 0.1 – 407 Pa. Further shearing has led to pseudoplastic flow region reflected in superposition of up-curve and down-curve. Above 483 Pa the system becomes thixotropic. Herewith, the thixotropy degree T is almost equal to the rheopexy degree R (*Table 1*). In turn, such a structural transition could be explained as follows. It is known that polymer solution represents three-dimension amorphous-crystalline system with high elastic properties [66, 69-71]. But individual molecules, their segments and microfibrils look spherical-shape coils and are in Brownian motion. When the system is undergone to low shearing, the elastic deformation of the initial network takes place: the coils partially overlap and form molecular linkage. This process is manifested in shear thickening region on viscosity profile (*Fig. 1*) and corresponds to dilatant properties of the system. Thus, the shear rate region where the viscosity increases is named an interval of structure reinforcement and formation; and Vd value corresponds to yield stress of initial structure. Herewith, the system shears like individual unit. According to the flow curves (*Fig. 1*), the beginning of initial structure damage is expressed in the rheopexic hystersis loop. Further shearing above Vd led to pseudoplastic flow region due to disrupting of cross links and transition to the regime of layered flow [72]. In the pseudoplastic region, the system is in equilibrium state because of balance between recovery and destruction processes. Further increased shear deformation leads to difference in shear rates between longitudinal molecular layers and the regions of intermolecular bonds appear. Co-existing of molecular associates with multiple bonds which can deform elastically so that the instantaneous local bonding is possible. Besides viscosity decreasing takes place due to thixotropy.

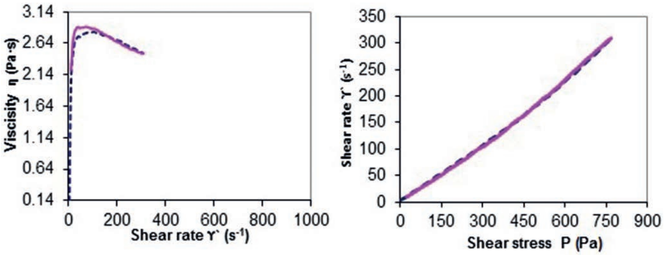

Fig. 1 *Viscosity profiles and flow curves of PP1 sample*
1. ábra *Viszkozitási profilok és folyási görbék a PP1 jelű mintánál*

3.2 Rheology of plasticized polymer solutions

In general, different concentration of DBP has an ambiguous influence on rheological properties of plasticized solutions and leads to various character of structuration. It was found that all solutions have thixotropic structural state and were shear thickened at low shear rates (*Table 1*).

Addition of 3.75, 5, 8.75, 17.5, 18.75, 20.8, 22.5, 25 and 30 m% of DBP resulted information of system structuring similarly to PP1. *Fig. 2* shows that the solutions PP3, PP4, PP6, PP11, PP12, PP14, PP16, PP17 and PP18 were successively in three structural states – rheopexic, pseudoplastic and thixotropic. The presence of plasticizer has led to viscosity η_τ decreasing. At the same time, for the sample PP14, increase of the viscosity value from 2.11 to 2.13 Pa·s was observed. Moreover, the DBP gives the Vd mean value of 25 – 30 s^{-1} (*Table 1*). It was also found that for the plasticized solutions with three structural states, the strength can be determined by thixotropy degree (*Fig. 3*). The increasing of T from 0.000001 to 0.0016 MPa/s almost does not affect the systems strength but further T rising to 0.006 MPa/s has led to abrupt lowering of strength and decreasing of viscosity η_τ almost by four times (PP16, 22.5 m% of DBP).

Discussed structural features could be explained as follows. The polymer systems with three structural states are disrupted thixotropic after passing through the previous states because of lower linearity and bigger size of polymer molecule and its similarity to a coil. Therefore, for the rheopexic and pseudoplastic states the orientation and layer-wise structural elements appear to be transformed to the thixotropic state.

It was established that addition of 2.5, 10, 11.25, 12.5, 20, 21.7 and 40 m% of DBP resulted in thixotropic solutions (*Fig. 4*). The decrease of viscosity η_τ was observed as well. However, the presence of 10 m% of plasticizer (PP7) increases viscosity η_τ from 2.11 up to 2.20 Pa·s. In general, the plasticizing leads to Vd value growth in average 20 – 25 s^{-1} (*Table 1*). This structural state could be explained as follows. The thixotropy phenomenon means disrupting of initial three-dimensional network structure under increased shearing accompanied with viscosity decrease for entire range of applied shear rates [66]. In the case of PP2, PP7, PP8, PP9, PP13, PP15 and PP19 solutions, the disrupting of initial structure begins from Vd shear rate: i.e. the initial three-dimensional structure after hardening within shear thickening region followed by two-dimensional layering in the Newtonian flow region ΔVn, gradually transforms to the one-dimensional structure. The absence of rheopexy and pseudoplasticity can be explained by polymer texture originating from linearity of EC macromolecule adsorbing the DBP. Thus, the orientation of initial layered structure takes place due to shearing.

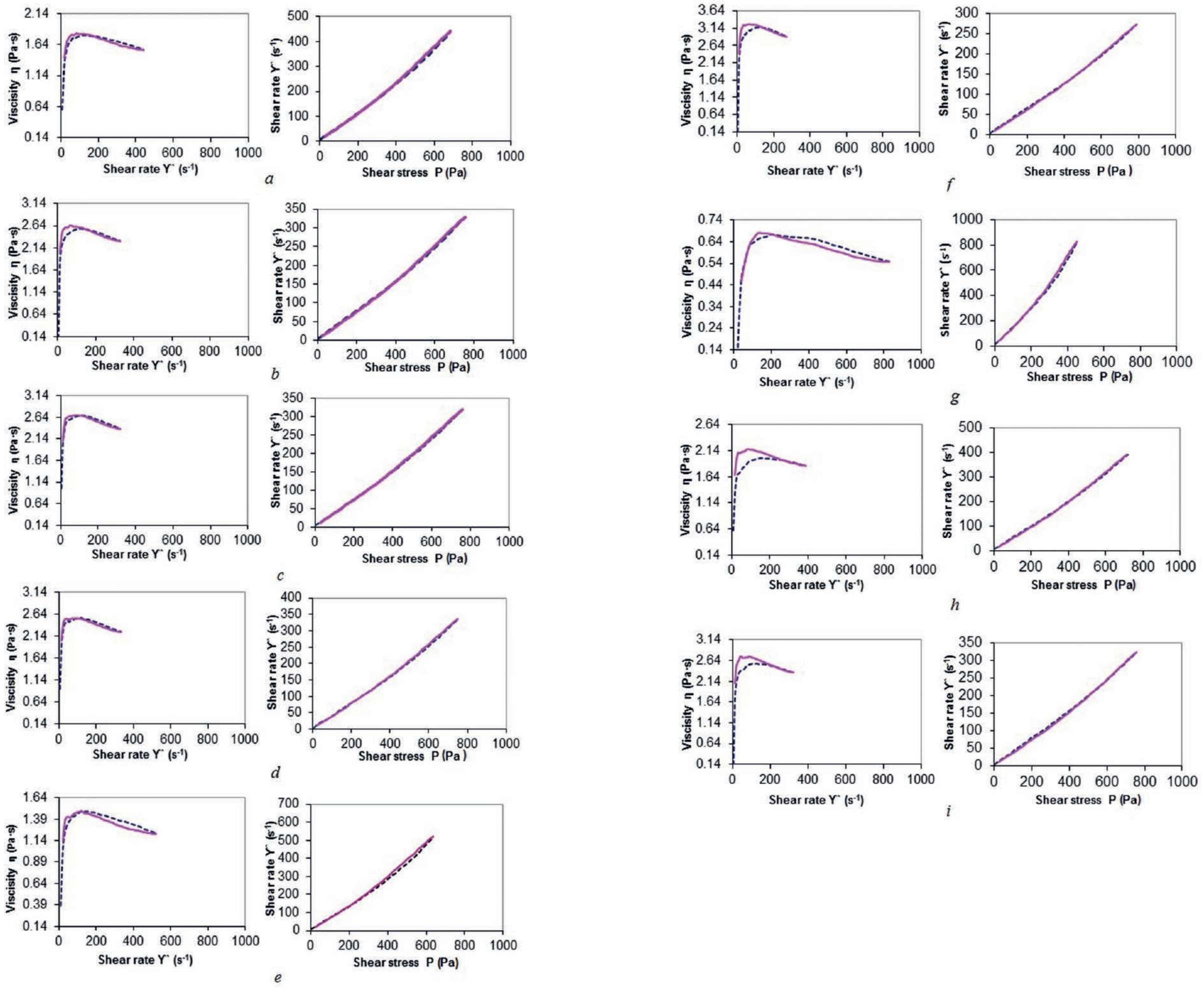

Fig. 2 Viscosity profiles and flow curves of plasticized solutions with three structural states (rheopexic, pseudoplastic and thixotropic)
2. ábra Viszkozitási profilok és folyási görbék a képlékenyített oldatok három szerkezeti állapotára vonatkozóan (reopexikus, pszeudoplasztikus és tixotróp)

Solution	DBP content, wt.%	Viscosity η_τ, Pa·s	Strenght stress, Pa	Dilatent flow Vd, s^{-1}	Maximal viscosity η_{max}, Pa·c	Newtonian flow end Vn_2, s^{-1}	Length of Newtonian region, ΔVn, s^{-1}	Thixotropy degree T, MPa/s	Dilatancy degree R, r.u.	Rheopexy degree R, MPa/s	EDSD, r.u.	Pseudoplastic flow start, Pa
PP1	0	2.11	766	78	2.81	108	30	0.001	0.33	0.001	2.12	407
PP2	2.5	1.44	694	108	1.96	129	21	0.006	0.36	0	1.58	0
PP3	3.75	1.33	686	117	1.79	139	22	0.003	0.35	0.001	2.00	305
PP4	5	1.83	753	109	2.58	130	21	0,001	0.41	0.001	2.68	363
PP5	7.5	1.53	717	121	2.12	148	28	0.004	0.39	0	2.19	25
PP6	8.75	2.07	759	106	2.68	144	38	0.002	0.29	0.000	2.03	242
PP7	10	2.20	784	103	3.19	117	14	0.004	0.45	0	2.54	0
PP8	11.25	1.05	595	116	1.40	130	14	0.012	0.33	0	0.92	0
PP9	12.5	1.29	649	99	1.68	123	24	0.011	0.30	0	1.05	0
PP10	15	1.46	732	172	2.18	189	17	0.000	0.49	0.003	4.50	0
PP11	17.5	1.91	750	86	2.54	127	41	0	0.33	0.000	2.17	261
PP12	18.75	1.08	636	136	1.46	162	26	0.006	0.35	0.000	1.65	164
PP13	20	1.59	709	108	2.15	127	19	0.010	0.35	0	1.40	0
PP14	20.8	2,13	789	130	3.18	0	0	0.001	0.49	0.001	3.75	435
PP15	21.7	1.05	684	100	1.92	132	33	0.010	0.83	0	2.35	0
PP16	22.5	0.46	453	198	0.67	0	0	0.006	0.48	0.000	1.75	134
PP17	25	1.40	718	146	2.00	165	19	0.000	0.43	0.004	4.00	538
PP18	30	1.82	757	109	2.57	133	25	0.000	0.41	0.002	3.41	535
PP19	40	1.88	744	77	2.53	110	33	0.004	0.35	0	1.86	0

Table 1 Composition and rheological properties of two- and three-component polymer solutions
1. táblázat Két- és háromkomponensű polimer oldatok összetétele és reológiai jellemzői

The solution PP5 (7.5 m% of DBP) was the polymer system with two structural states: in the range of shear strain of 25 – 173 Pa the pseudoplastic flow has been observed and further shearing led the system to transform into thixotropical one (*Fig. 5*). In this case the plasticizer addition also led to viscosity η_τ decreasing from 2.11 to 1.53 Pa·s and Vd increasing up to 121 s^{-1} (*Table 1*).

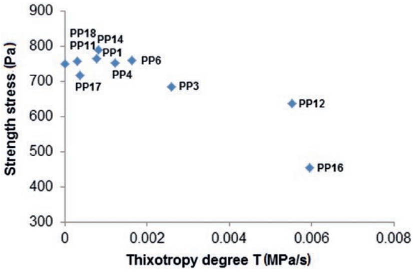

Fig. 3 *Strength dependence of thixotropy degree for plasticized solutions with three structural states (rheopexic, pseudoplastic and thixotropic)*
3. ábra *Szilárdság függése a tixotrópia fokától a képlékenyített oldatok három szerkezeti állapotára vonatkozóan (reopexikus, pszeudoplasztikus és tixotróp)*

Addition of 15 m% of DBP (PP10) corresponds to formation of two structural states in the system. In the shear stress range 25 – 520 Pa the solution was rheopexic but the further shearing up to 732 Pa forced the systems transform into thixotropical one and abide the pseudoplastic structural state (*Fig. 6*). The viscosity η_τ decreasing from 2.11 to 1.46 Pa·s and Vd increasing from 78 to 172 s^{-1} were observed (*Table 1*).

Understanding of whether the plasticizer provides one or several structural states during shearing needs to establish what the dissolved polymer is. It is known that polymer chains have some flexibility because of which macromolecules are folded [55, 73]. Thus, polymer has loosen structure with large intermolecular voids (*Fig. 7*, 1st stage). On the first stage of dissolving the swelling of polymer takes place – solvent molecules diffuse into the polymer and fill the intermolecular voids. Further increasing of solvent volume leads to macromolecules moving apart because of changed gyration radius and distance between the centers of mass. Herewith, the continuity of polymer body is retained. However, an intensification of swelling leads to appearance of antiparallel separate segments of macromolecule referred as crystallites [74]. At the same time the crystallites exist in large quantities and alternating with amorphous regions form the center of elementary fibril [54] (*Fig. 7*, 3rd stage). The external part of elementary fibril is paracrystalline zone with large surface energy. Thus, elementary fibrils are prone to lateral aggregation with formation of fibrils (*Fig. 7*, 4th stage). But further stirring and, therefore, exceeding the optimal swelling time results in destruction of polymer continuity and molecules begin to tear off passing into the solution.

However, if plasticizer would be added before the final transition of polymer to the solution, the molecule conformation changes simultaneously with segments moving apart due to DBP adsorption on EC molecule [58] (*Fig. 8*, 2nd stage). Herewith the smaller crystallites are formed because of reducing the number of antiparallel macromolecule segments. Thus, the achieved plasticized solution will be predominantly

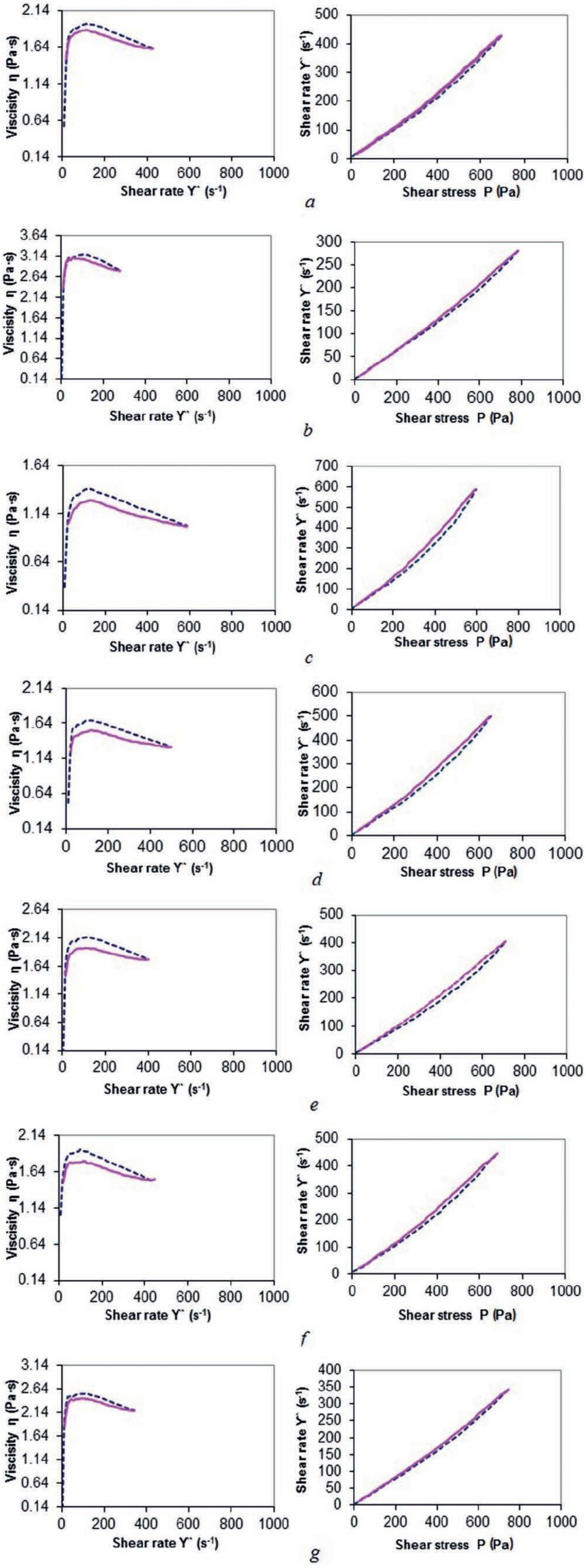

Fig. 4 *Viscosity profiles and flow curves of plasticized solutions with thixotropic structural state*
4. ábra *Viszkozitási profilok és folyási görbék a képlékenyített oldatok tixotróp szerkezeti állapotára vonatkozóan*

amorphous system with some concentration of crystallites. But plasticizer addition does not exclude the possibility of EC macromolecule disrupting to smaller parts (*Fig. 8*, 3rd stage) on dissolving. The EC macromolecule has so-called weak points (authors of [55] assume the presence of leisure chains without hemiacetal bond $C_{(1)} \rightarrow C_{(5)}$ together with closed pyranose cycles).

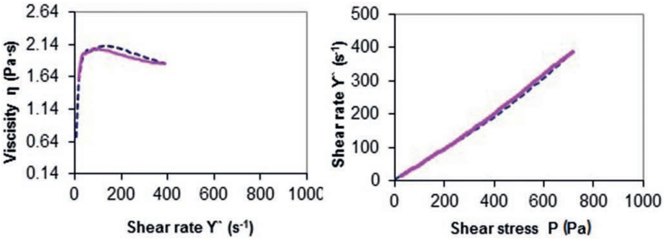

Fig. 5 *Viscosity profile and flow curves of plasticized solution PP5 with pseudoplastic and thixotropic structural states*
5. ábra *Viszkozitási profil és folyási görbék a PP5 jelű képlékenyített oldat pszeudoplasztikus és tixotróp szerkezeti állapotára vonatkozóan*

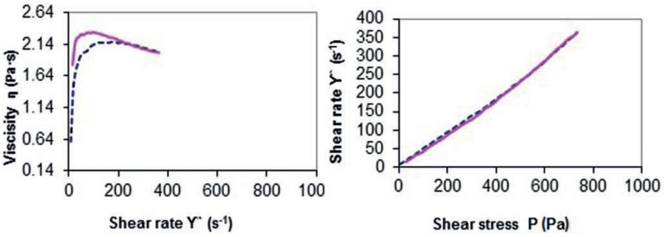

Fig. 6 *Viscosity profile and flow curves of plasticized solution PP10 with rheopexic and thixotropic structural states*
6. ábra *Viszkozitási profil és folyási görbék a PP10 jelű képlékenyített oldat reopexikus és tixotróp szerkezeti állapotára vonatkozóan*

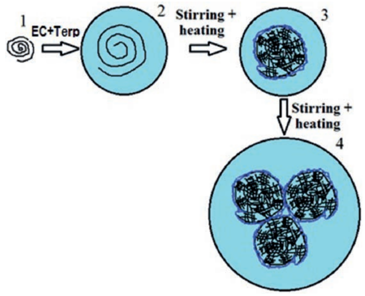

Fig. 7 *Stages of interaction in the initial solution EC+Terp*
7. ábra *A kölcsönhatások szakaszai a kezdeti EC+Terp oldatban*

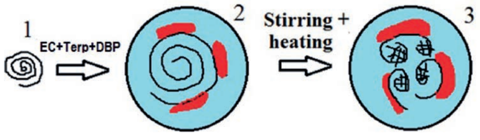

Fig. 8 *Stages of interaction in plasticized solution EC+Terp+DBP*
8. ábra *A kölcsönhatások szakaszai a képlékenyített EC+Terp+DBP oldatban*

So, plasticizer addition leads to formation of three-dimensional structure with certain physical-mechanical properties as a result of plasticized EC macromolecule conformation. In general, the specific change of some rheological characteristics is comprehensive. In particular, Vd increases and η_τ decreases that is entirely consistent with features of structure formation during plasticizing. Formed small crystallites affect as particulate-reinforcing phase. The viscosity η_τ decreases due to lowering of strength stress of structure (*Fig. 9*). However, for PP16 (22.5 m% of DBP) the viscosity η_τ decreases in almost 4 times because of the lowest strength value and possible bimodal distribution of crystallites [75].

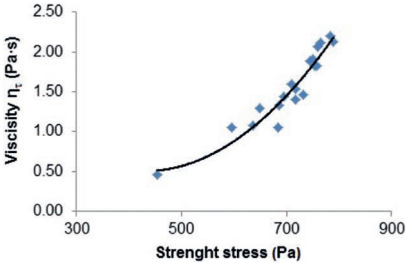

Fig. 9 *Viscosity η_τ dependence on strength*
9. ábra *Viszkozitás η_τ szilárdságfüggése*

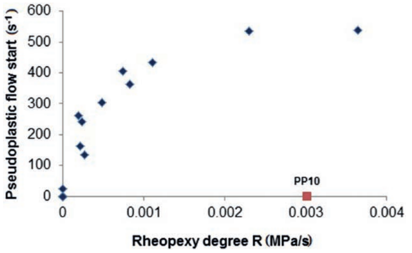

Fig. 10 *Rheopexy degree versus pseudoplastic flow start*
10. ábra *Reopexikusság foka és pszeudoplasztikus folyás kezdete*

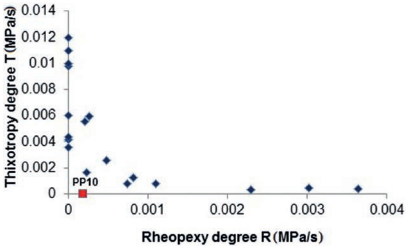

Fig. 11 *Rheopexy degree versus thixotropy degree*
11. ábra *Reopexikusság foka és tixotrópia foka*

It was established that the investigated solutions demonstrate causal link between structural states formed. In particular, the rheopexy degree R determines the start of pseudoplastic flow and thixotropy degree T. *Fig. 10* shows that the R increasing from 0 to 0.0015 MPa/s leads to pseudoplastic flow start at higher shear rates (~ 500 s^{-1}). But further increase in R does not effect on system transforming into two-dimensional state. Such a tendency was observed almost for all solutions (the PP10 was exception only because of absence of pseudoplastic flow region). In turn, the R value grows up to 0.0015 Mpa/s and leads to abrupt decrease in T. Further increase in R does not affect the system transforming into one-dimensional state. The only exception concerns the PP10 similarly to dependence shown in *Fig. 10*. In both cases, the PP10 exception can be explained as follows. Due to the fact that the initial structure of all the solutions is disrupted and restored under increased shear rates, it seems to be true that the thixotropy degree T decreases with increasing of the rheopexy degree R (*Fig. 11*). Besides, *Table 1* shows that for the PP10 the EDSD criteria value is the highest one. Thus, in the PP10 case the destruction processes dominate over recovery processes without equilibrium state.

4. Conclusions

The investigated polymer solutions were three-dimensional structured systems which were shear thickened at low shear rates and maintained the thixotropic structural state under high shear rates. It was found that the initial polymer solution EC+Terp was successively in three structural states: rheopexic, pseudoplastic and thixotropic. Herewith, the R was almost equal to T because of equal recovery and destruction processes. However, addition of different amount of plasticizer had an ambiguous influence on rheology of solutions and led to formation of transient polymer network with a complicated character of structuration because of the features of interaction in the polymer - plasticizer system. It was established that the plasticization results in changing of EC molecules conformation and simultaneous breaking of the polymer continuity due to DBP adsorption on EC macromolecule. Herewith, the formation of smaller crystallites took place. Besides, the investigated solutions showed causal link between structural states. In particular, the rheopexy degree R determines pseudoplastic flow start and the thixotropy degree T.

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