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Rheological behaviour of some magnetic polymer composites

F. MUSTATA*, N.TUDORACHI
Institute of Macromolecular Chemistry "P. PONI", Aleea Gr. Ghica Voda, 41A, 700487, Iasi, Romania

The investigation reports the flow properties of concentrated solutions of 2-Ethylhexyl acrylate/Styrene/Acrylic acid, copolymers modified with magnetic particles of Fe_3O_4, as functions of concentration and shear rate. The measurements were carried out by means of a rotary viscometer equipped with coaxial cylinder device at shear rates varying between 1 and 1310 sec^{-1}, temperature range 20 °C to 40 °C, and filler content varying between 15% and 50% (w/w), reported to the weight mixture. The rheological parameters evaluated on the flow are the consistency index, the flow index and the yield stress. The literature rheological models were employed to investigate the shear stress dependence with the shear rate.

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Key words: Acrylic copolymers, Magnetic iron oxide powder, Rheological behaviour

1. Introduction

Magnetic recording media such as floppy disk, audio, video and digital tapes consist of a thin layer of fine magnetic particles, homogenously dispersed into a nonmagnetic solid polymer material, coated on polymer support (usually polyester type). The common method to obtain these products consists in coating of magnetic polymer composite on the solid substrate of polyester type followed by solvent evaporation. The ultimate properties of the obtained products depend on the quality of the magnetic particles, the chemical structure of the polymer and solvent and the coating process.

The understanding of the rheological behaviour of the magnetic suspension can help the control of coating operations and have great importance in obtainment of high quality final products.

It is well known that the properties of the homogeneous suspension depends on the dimension and form of particles, on their density, concentration, viscosity and hydrodynamic conditions. The continuous phase can exhibit Newtonian or non-Newtonian behaviour, that becomes more complicated in the presence of the solid phase. The common suspension obtained from Newtonian medium show Newtonian behaviour at low concentration of solids, but with solid concentration increase, the non-Newtonian behaviour appears. The presence of magnetic particles, in the suspension structure induces a non-Newtonian behaviour unaffected by the liquid characteristics.

The are many studies concerning the rheological aspects of magnetic suspensions but most of them discussed the suspensions in Newtonian medium (ethylene glycol, silicone oil, dioctyl phthalate, hydrocarbon oil, etc.) [1-10]. A survey of literature data, show a few references, that describe the rheological behaviour of polymeric magnetic suspensions [6, 11-15].

In the present work, we report the results obtained in the synthesis and characterization of some new acrylic copolymers, which will be further used as binders in magnetic suspensions, with possible utilization in manufacturing of magnetic tapes or disks. Also, the rheological behaviour of the obtained suspension with magnetic Fe_3O_4 particles in the composition was investigated.

2. Experimental

2.1. Materials

2-Ethylhexyl acrylate (2-EHA), styrene (St), acrylic acid (AAc), benzoyl peroxide (BzO), cyclohexanone (CH_x), were used as received. The magnetic particle (Fe_3O_4), were obtained from a commercial source (Sinteza Oradea, Romania), and were used without purification. The black powder has acicular form with the aspect ratio 6.5/1, with of 0.6 μm length and 5.25 g/cm^3 density.

2.1.2. Suspension preparation

The sample suspensions were prepared by mixing Fe_3 O4 powder with the polymer solution at various weight ratio polymer/iron oxide/solvent and ball milling at room temperature for two days.

2.2. Measurements

Average molecular weight was obtained using gel permeation chromatography (GPC) with chloroform as mobile phase. Infrared spectra (FT-IR) were recorded using Bruker Vortex 70 spectrophotometer on KBr pellets. ^{1}H-NMR spectra were obtained on an Avance DRX 400 (Bruker, Germany) at 50 °C, using chloroform as solvent and tetramethylsilane as internal standard (NMR chemical shift were expressed in ppm). The glass transition temperature values were measured by means of Differential Scanning Calorimeter Perkin Elmer-Pyris Diamond analyser at temperature range -60 to 100 ^oC with a 20 ^oC/min heating rate. The particle density was measured using the picnometry method. The particle size was obtained using a Mastersizer 2000 (ver.5.31) Malvern Instruments (England). The morphological inspection of the blends was performed by means of a MICROS-MCD500 microscope (Austria) at magnification 10x.

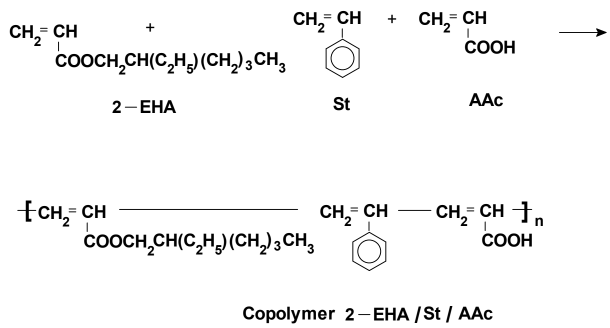
The rheological measurement was performed using a Rheotest RV2 (Germany) coaxial cylinder viscometer. The viscometer has a torquemeter, which can be driven at 12 discrete rotational speeds with shear rate ranging from 0.15 to 1310 s^{-1}. The temperature sample was maintained at constant temperature using an Ultrathermostat U10 (Germany) with a $\pm$ 0.01 ^oC precision. The measurements were performed at 20, 30, 40 ^oC temperatures at which is possible that coating operation can take place. After the test sample was loaded into cylinder, was heated 15 min at the test temperature and sheared at a maximum shear rate to obtain a homogenous dispersion. The torques were recorded after it attained a constant value. Shear rates were decreased stepwise and the torque was measured for each step. For each temperature and for each weight ratio a new sample was used.

2.3. Synthesis of 2-EHA/St/AAc copolymers

A copolymer with 2-EHA/St/AAc in composition was prepared by a standard procedure using classical radical polymerisation process at various molar ratios of monomers. Reaction conditions and some physical-chemical characteristics are presented in Table 1. In a representative experiment, (Table 1) a 0.5 L four- necked round bottomed flask equipped with thermometer, mechanical stirrer, water bath and dropping funnel is charged with 184.28 g (1 mol) 2-EHA, 83.2 g (0.8 mol) St, 7.3 g (0.1 mol) AAc and 50 ml cyclohexanone. The reaction mass was heated at 80-85 ^oC, maintained 15 min at this temperature, and 3g (1 % based on the monomer weight) BzO dissolved in 20.8 g (0.2 mol) St was added in over 2 h. Then, the reaction was continued at this temperature for 5 h. By regular intervals, the viscous solution was diluted with another 50 ml of cyclohexanone. The resulting copolymer solution was clear with a slight yellow colour (yield 95 %).

3. Results and discussion

The chemical reaction between 2-EHA, St, AAc at 80-85 ^oC is presented in Scheme 1. The choice of 2-EHA and AAc confers to the copolymers, adhesivity to polymer substrate, and to iron oxide powder and St confers rigidity to the obtained film. The chemical structure was confirmed by IR and ^{1}H-NMR spectroscopy. In the IR spectra (Fig. 1), the characteristic bands are obtained at 2860-2980 cm^{-1} (specific to CH, CH_2, CH_3 groups located in the 2-EHA monomers, at 1624 cm^{-1} (specific to C-C links of St aromatic ring) and at 1730 and 1160-1260 cm^{-1} specific to the ester groups. At 650-760 cm^{-1} appear the specific bands characteristic to p-substituted benzene.



Scheme 1. Copolymer synthesis.

Table 1. Initial chemical composition, reaction conditions and some physical properties.

Sample	Composition		
	Monomers	(parts)	
A	2-EHA	1	1
	Styrene	1	2
	AAc	0.1	0.1
B	Initiators (BzO)	0.03	0.03
C	Cyclohexanone	1	1
D	Temperature ^oC	80-85	80-85
E	Time (h)	6	6
F	Dry content	66%	66%
H	Molecular weight Mn Mw Mw/Mn	 16200 32000 1.972	 22400 38300 1.71
I	Glass transition temperature ^oC	-3	3

Mn-Number average molecular weight,
Mw- Gravimetric average molecular weight,
Mw/Mn- polydispersity index

The ^{1}H-NMR spectra, confirm the structure of the obtained copolymers. The major signals are located in the range of 0.9 to 2.15 ppm specific to vibrations of CH, CH_2, CH_3 groups and in the range of 6.7-7.3 ppm specific to aromatic protons.

As can be seen in Table 1, the molecular weights and the glass transition temperature is different and depends on styrene content, the copolymer with more styrene content has higher molecular weights and glass transition temperature.

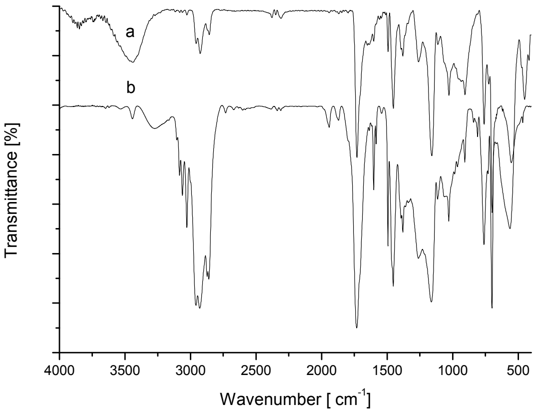


Fig 1. IR spectra of copolymers: (a) copolymer (2-EHA/St/AAc- 1/2/0.1)/iron oxide (1/1) (b) copolymer (2-EHA/St/Aac-1/1/0.1).

Typical microscopic structures of the iron oxide films are illustrated by photomicrographs shown in Figs. 2-5. The dry resin blends are composed of a continuous phase, in which is dispersed the iron oxide powder. At high concentration of iron oxide powder (>33 %) there is a good distribution of iron oxide particles in the blends. Generally, the iron oxide powder particles are not evenly distributed in the continues phase. It can be remarked that for higher iron oxide content in copolymer/iron oxide blends the iron oxide powder is relatively uniform distributed in the continuous phase (Figs. 3-5).

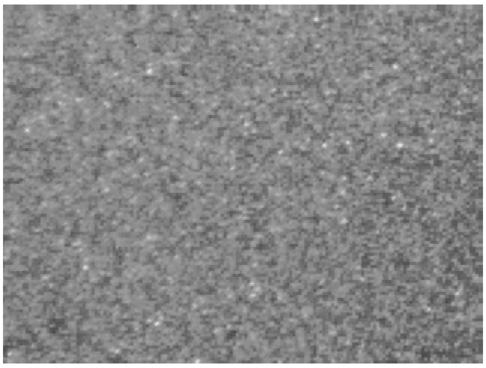


Fig. 2. Commercial magnetic film, magnification 10x.

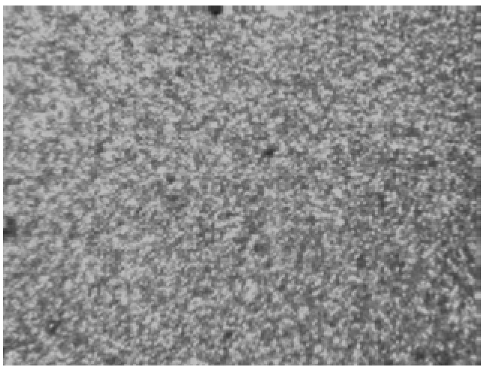


Fig. 3. Magnetic film obtained from 2EHA/St/AAc (1/1/0.1) copolymer at copolymer / iron oxide ratio (1/1.5), magnification 10x.

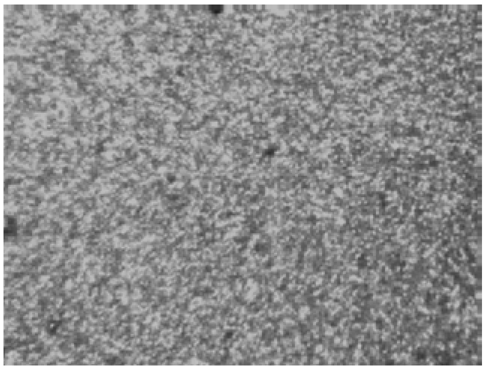


Fig. 4. Magnetic film obtained from 2EHA/St/AAc (1/2/0.1) copolymer at copolymer / iron oxide ratio (1/1), magnification 10x.

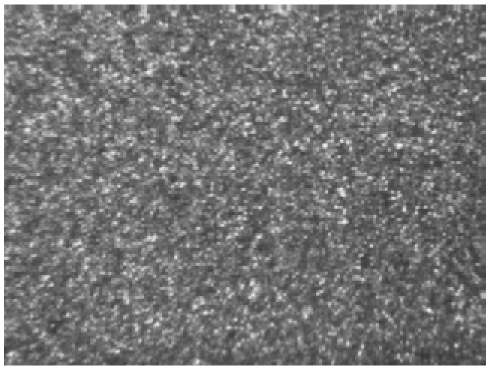


Fig. 5. Magnetic film obtained from 2EHA/St/AAc (1/2/0.1) copolymer at copolymer / iron oxide ratio (1/1.5), magnification 10x

Microscopic observation indicates that the adhesion between particles and continous phase is good, evidenced by the absence of gaps in the boundary regions of the two phases. Adhesion between phases is an important feature because it has a critical influence on the mechanical properties of the polymer blends.

The polymer solutions were characterized before adding the iron oxide powder by their rheological behaviour. The rheological behaviour of concentrated polymer solutions depends on polymer molecular weights, chemical structure and the solvent type. The literature data show that the viscosity of concentrated polymer solutions is function of molecular weights and two constants [16-18].

$$\eta = KM^{\alpha} \quad (1)$$

where: K-constant depend of polymer and solvent type; M- molecular weight and $\alpha = 3.4$

The apparent viscosity was evaluated using the following equation:

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (2)$$

where: τ - is the shear stress and $\dot{\gamma}$ - is the gradient of shear rate.

Because, the apparent viscosity is a function of the shear rate, we use the consistency index (zero shear rate viscosity) to characterize the polymer solution. The value of consistency index and the flow index for copolymer solutions were obtained using the power law model (Table 2), which can characterize the rheological behaviour [16, 17]. In Figs. 6 and 7, we present the variation of consistency index versus concentration for the two obtained polymers. The variation of obtained consistency index versus concentration is good approximated by equation 1 and is confirmed by literature data [16-18]. Following up the variation of viscosity versus shear rate at constant temperature, it can be seen that the viscosity decrease with shear rate increase. The fact that the flow index is lower than 1 suggests that the solution has a non-Newtonian behaviour of pseudoplastic type.

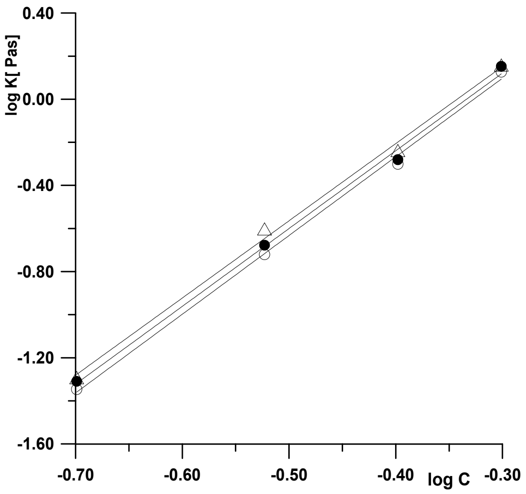


Fig. 6. Consistency index as a function of concentration at temperature: (△) 40 °C; (●) 30 °C; (○) 20 °C, for 2-EHA/St/AcAc (1/1/0.1) copolymer in cyclohexanone

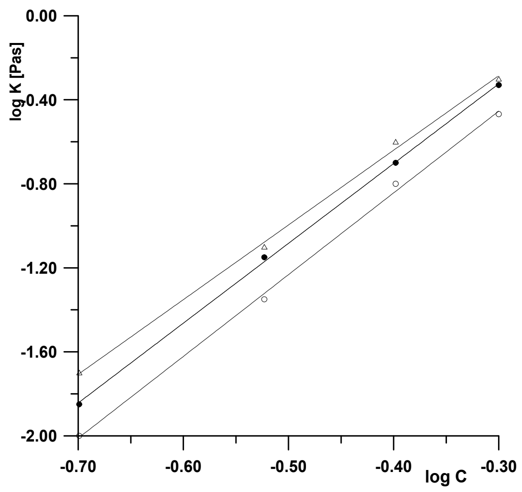


Fig. 7. Consistency index as a function of concentration at temperature: (△) 40 °C;(●) 30 °C ; (○) 20 °C, for 2-EHA/St/AAc (1/2/0.1) copolymer in cyclohexanone.

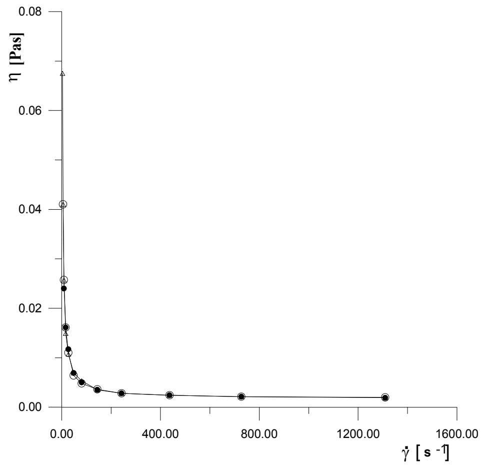


Fig. 8. Viscosity as a function of shear rate for 2-EHA/St/AcAc (1/1/0.1) copolymer/ cyclohexanone/iron oxide (1/1/1) ratio, at temperature: (△) 40 °C; (●) 30 °C; (○) 20 °C.

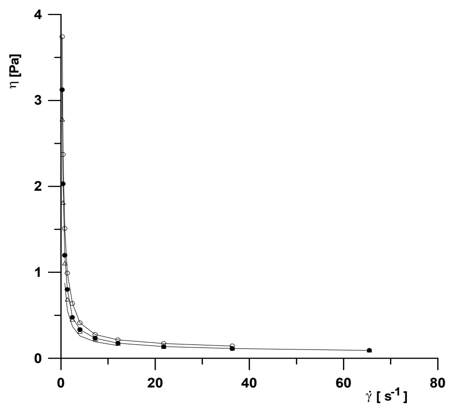


Fig. 9. Viscosity as a function of shear rate for 2-EHA/St/AAc (1/1/0.1)copolymer/cyclohexanone / iron oxide (1/1/2) ratio, at temperature: (△) 40 °C; (●) 30 °C; (○) 20 °C.

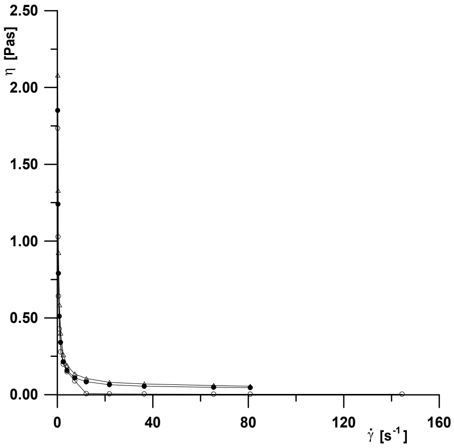


Fig. 10. Viscosity as a function of shear rate for copolymer 2-EHA/St/AAc (1/1/0.1) at copolymer/cyclohexanone/ iron oxide (1/1/1.5)ratio at temperature : (○) 40 °C; (●) 30 °C ; (△) 20 °C.

Table 2. Rheological models.

Model	Mathematical equations	Material constants
Mooney	$\mathrm{Ln}(\frac{\eta}{\eta_0})=[\eta]\phi/(1-\frac{\phi}{\phi_\infty})$	η_o,φ_∞
Ostwald de Waele	$\tau = K_1 \dot{\gamma}^{n}$	K_1,n
Plastic Bingham	$\tau = \tau_o + K_2 \dot{\gamma}$	K_2, τ_o
Casson	$\tau^{0.5} = \tau_o + K_3 \dot{\gamma}^{0.5}$	K_3, τ_o
Extended Casson	$\tau^{0.5} = \tau_o + K_4 \dot{\gamma}^{0.5n}$	K_4,n, τ_o

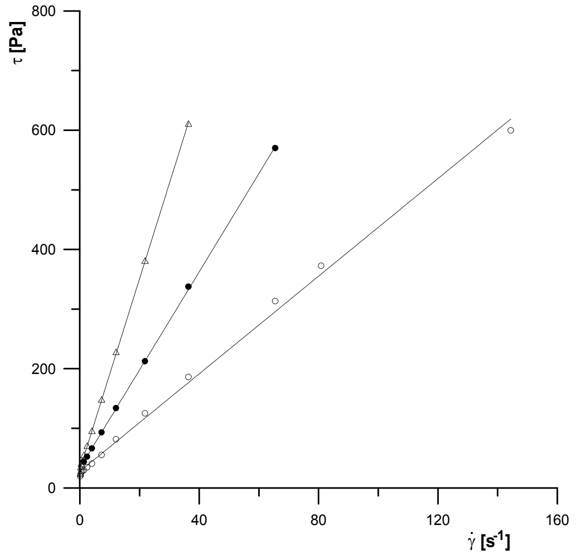


Fig. 11. Variation of shear stress versus shear rate for copolymer (2-EHA/St/AAc-1/2/0.1) at copolymer/ cyclohexanone/iron oxide(1/1/2) ratio and temperature: (○) 40 °C; (●) 30 °C; (△) 20 °C.

The experimental data were processed using the power law model, and the consistency index and flow index were obtained. From the data presented in Tables 3 and 4 it can be seen that the flow indices decrease with concentration increase but don't differ much with temperature increase.

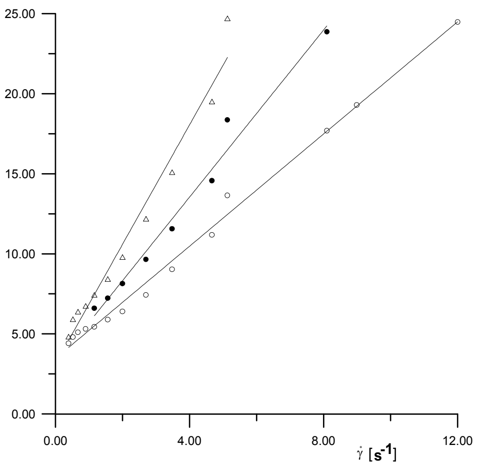


Fig. 12. Variation of shear stress at 0.5 power versus shear rate at 0.5 power for copolymer 2-EHA/St/AAc (1/2/0.1) at copolymer/cyclohexanone/iron oxide (1/1/2) ratio and temperature: (○) 40 °C; (●)30 °C; (△) 20 °C.

The rheological characteristic of particle suspensions, which contain iron oxide clusters, is shear thinning. Under the action of shear stress, o lot of clusters are deformed and destroyed, and the liquid included is released. Consequently, the suspensions become less viscous. To describe the rheological behaviour of the suspensions some mathematical models are used (Table 2). In order to investigate the shear rate dependence versus viscosity, we fitted the measured viscosity to the mathematical models given in Table 2. The randomly chosen experimental data are presented in Figs. 8-12 and in Tables 5-8, for iron oxide particle suspensions using Bingham and Casson rheological models. According with temperature and iron oxide content at which the tests were carried out, a lot of straight lines were obtained. These lines indicate that the finite yield stress exists for iron oxide suspensions and with iron oxide concentration decrease, the intercept related to the yield stress approaches to zero. The fact that the curves are present as straight lines suggests that the mathematical models approximated well the rheological behaviour. Extrapolation of these lines to the shear stress axis gives the yield stress and shear viscosity for Bingham model (Table 5 and 6) and the square roots of the yield stress and the slope the square roots of the limiting shear viscosity for Casson model (Table 7 and 8).

Table 3. Variation of the flow index and consistency index with temperature and concentration of copolymer solutions 2-EHA/St/AAc (1/1/0.1)

Temperature °C	Concentration (polymer/solvent) (w/w)							
	50		40		30		20	
	n	k	n	k	n	k	n	k
20	0.85	1.44	0.73	0.578	0.72	0.25	0.41	0.051
30	0.74	1.42	0.71	0.524	0.70	0.21	0.40	0.049
40	0.73	1.34	0.71	0.502	0.70	0.19	0.39	0.045

Table 4. Variation of the flow index and consistency index with temperature and concentration of copolymer solutions 2-EHA/St/AAc (1/2/0.1)

Temperature ^oC	Concentration (polymer/solvent) (w/w)							
	50		40		30		20	
	n	k	n	k	n	k	n	k
20	0.84	0.50	0.75	0.25	0.75	0.081	0.51	0.020
30	0.78	0.47	0.74	0.19	0.74	0.072	0.53	0.014
40	0.77	0.38	0.72	0.16	0.71	0.044	0.52	0.010

n-flow index
k-consistency index (Pas)

Table 5. Variation of the Bingham viscosity and yield stress with temperature and concentration for iron oxide blends with 2EHA/St/AAc(1/1/0.1) copolymer

Tempe-rature (^oC)	Concentration (cyclohexanone/copolymer/iron oxide) (w/w/w)							
	4.6/1/1		1/1/1		1/1/1.5		1/1/2	
	k	τ_o	k	τ_o	k	τ_o	k	τ_o
20	0.88	0.98	1.62	1.34	5.34	2.75	9.95	7.50
30	0.61	0.76	1.38	1.21	4.46	2.28	10.60	5.95
40	0.55	0.65	1.0	1.12	3.89	1.91	12.58	5.38

Table 6. Variation of the Bingham viscosity and yield stress with temperature and concentration for iron oxide blends with 2EHA/St/AAc(1/2/0.1) copolymer

Tempe-rature ^oC	Concentration (cyclohexanone/copolymer/iron oxide) w/w							
	4.6/1/1		1/1/1		1/1/1.5		1/1/2	
	k	τ_o	k	τ_o	k	τ_o	k	τ_o
20	0.53	1.87	1.82	2.60	7.76	4.87	15.98	31.05
30	0.42	1.89	1.54	2.45	6.43	4.05	10.65	29.5
40	0.32	1.98	1.32	2.36	5.67	3.36	4.09	27.75

k- Bingham viscosity (Pas)
τ_o-yield stress (Pa)

Table 7. Variation of the square roots of the yield stress and the square roots of the limiting shear viscosity with temperature and concentration for iron oxide blends with 2EHA/St/Aac (1/1/0.1) copolymer

Tempe-rature (^oC)	Concentration (cyclohexanone/copolymer/iron oxide) (w/w/w)					
	1/1/1		1/1/1.5		1/1/2	
	$\eta^{0.5}$	$\tau_o^{0.5}$	$\eta^{0.5}$	$\tau_o^{0.5}$	$\eta^{0.5}$	$\tau_o^{0.5}$
20	0.11	1.16	0.54	1.66	0.72	2.74
30	0.10	1.10	0.50	1.51	0.64	2.43
40	0.09	1.06	0.45	1.38	0.54	2.32

$\eta^{0.5}$- the square roots of the limiting shear viscosity
$\tau_o^{0..5}$-the square roots of the yield stress

Table 8. Variation of the square roots of the yield stress and the square roots of the limiting shear viscosity with temperature and concentration for iron oxide blends with 2EHA/St/AAc (1/2/0.1) copolymer

Tempe-rature °C	Concentration (cyclohexanone/copolymer/iron oxide) (w/w/w)					
	1/1/1		1/1/1.5		1/1/2	
	$\eta^{0.5}$	$\tau_o^{0..5}$	$\eta^{0.5}$	$\tau_o^{0..5}$	$\eta^{0.5}$	$\tau_o^{0..5}$
20	0.56	1.87	0.78	3.40	3.13	3.47
30	0.51	1.36	0.66	3.01	2.50	3.14
40	0.47	1.28	0.55	2.87	1.74	3.02

$\eta^{0.5}$- the square roots of the limiting shear viscosity
$\tau_o^{0.5}$-the square roots of the yield stress

4. Conclusion

The iron oxide suspensions have a rheological behaviour of pseudoplastic type. The non-Newtonian character appears as a result of the formation of the aggregates between solid particles and the polymer chains linked by hydrogen bonds and magnetic forces. At high concentrations, the suspensions present yield stress, and with temperature increase and iron oxide concentration decrease, the yield stress tends to zero. The shear rate dependence on iron oxide suspensions viscosity for 2-EHA/St/AcAc copolymers is well described by Casson model.

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*Corresponding author: fmustata@icmpp.ro