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Rheological Properties of PVDF Solutions

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Abstract. The rheological properties of polyvinylidene fluoride (PVDF) solutions in N-methylpyrrolidone were studied using the rheometric method. It was shown that the viscosity of polymer solutions decreases non-linearly with increasing temperature. The viscosity of the N-methylpyrrolidone used as solvent remains practically unchanged. It was shown that solutions exhibit Newtonian behaviour at concentrations less than 7 wt.%. At higher concentrations, solutions exhibit properties of pseudoplastic fluid.

Keywords: liquids, structure, viscosity, rheological properties, Newtonian and non-Newtonian behaviour, polyvinylidene fluoride (PVDF), N-methylpyrrolidone, materials performance, temperature dependences.

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Introduction

The paper deals with the study of fundamental problem of fluid structure engineering. The basic and essential feature of the present paper is the research object — a suspension of functional piezo polymer and piezo polymer-based nano-composite suspensions. The ferroelectric, piezoelectric polymer PVDF is considered. Its spontaneous electric polarization varies between 3 and 7 $\mu c/cm^2$. One of the simple and effective methods of modifying the properties of functional materials is mechanical processing (compression/stretching) which leads to the accumulation of mechanical stresses in the material, crystal lattice distortions and deformations of chemical bonds. This approach is called the strain engineering [1,2]. Many studies have demonstrated the

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effectiveness of this approach in changing optical, magnetic, chemical (catalytic) and electrical properties. Low-symmetry ferroelectrics occupy an exceptional place among various available materials. By analogy with magnetic materials, they have two important properties: orientation of a spontaneous polarization vector (the total dipole moment of the system) can be changed by the direction of the external electric field and the ferroelectric-paraelectric phase transition at the Curie temperature. Unlike quantum dots and superparamagnetic particles, ferroelectrics show significant degradation of their functional properties which is explained by a violation of the balance of short-range and long-range forces of the system in the framework of the Landau-Devonshire-Ginzburg theory of ferroelectric effect [3].

It was experimentally shown in 2004 that the spontaneous polarization of epitaxially grown barium titanate film with a certain difference in the parameters of an elementary crystal cell can be 250 % above the spontaneous polarization of a bulk crystal [4]. Theoretical studies showed that this increase can be induced by mechanical deformation, in particular, by biaxial compression of the barium titanate film [5]. The strain engineering concept which consists in selecting systems with certain difference in the lattice parameters can significantly enhance the functional characteristics of low-dimensional ferroelectrics. However, this is only possible for thin films and two-dimensional systems. In the case of nanoparticles the situation is essentially different. Methods of chemical synthesis of monodisperse nanoparticles do not yet allow producing particles in the "stressed, deformed" state due to the passive role of ligands covering the surface [6]. Therefore, it is of interest to stabilize such polymer particles in viscous media and thus to create ensembles of particles periodically located in space and stabilized by interaction with the surrounding polymer molecules. This in turn can significantly affect the low-frequency rheological characteristics of nanosuspensions and be evidence of "solidification". Recently, there was great interest in the study of fluids that exhibit non-Newtonian behaviour [7–12]. Previously, it was shown that PVDF solutions mainly exhibit Newtonian behaviour [13–16]. In this work, a deviation from the Newtonian behaviour of PVDF solutions in N-methylpyrrolidone (NMP) was found at certain weight concentrations.

1. Experiment

1.1. Materials under study

Polyvinylidenefluoride(PVDF)

Polyvinylidene fluoride or polyvinylidene difluoride (PVDF) is a highly reactive thermoplastic fluoropolymer obtained by polymerization of vinylidene fluoride [17] (see Fig. 1). The chemical formula of polyvinylidene fluoride is $(C_2H_2F_2)_n$.

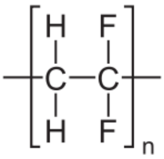

Fig. 1. The structural formula of the PVDF

The PVDF is a crystalline polymer of white or translucent colour with a molecular weight of over 100,000. The PVDF is a special plastic used in areas where the highest purity as well as resistance to solvents, acids, and hydrocarbons is required. Compared to other fluoropolymers, such as polytetrafluoroethylene (Teflon), PVDF has low density (1.78 g/cm^3). The polymer has high mechanical strength, wear and weather resistance as well as resistance to ionizing and ultraviolet radiation [18]. Besides, it also exhibits high chemical resistance and compatibility with thermoplastic materials. In industry, PVDF solutions are used to produce fluoroplastic membranes.

N-methylpyrrolidone

N-methylpyrrolidone (NMP) is an organic compound comprising of five-membered lactams (see Fig. 2). It is a colourless liquid but impure samples may look yellow. It also belongs to the class of dipolar aprotic solvents, such as dimethylformamide and dimethyl sulfoxide. It is mixed with water, and it is the most common organic solvent used in the petrochemical and plastic industries due to its volatility and ability to dissolve various materials including polymers.

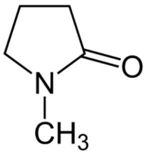

Fig. 2. The structural formula of the NMP

Its chemical formula is C_5H_9NO, molar weight is 99.133 $g{\cdot}mol^{-1}$, and density is 1.028 g/cm^3. The NMP is used for the extraction of certain hydrocarbons formed in the processing of petrochemical products, such as the reduction of 1,3-butadiene and acetylene. It is also used for the absorption of hydrogen sulfide from acid gases and hydrodesulfurization plants. N-methylpyrrolidone is used for dissolving a wide range of polymers.

Typically, polymers dissolved in NMP are used to treat the surface of electrodes or produce polymer electrolytes. The results of measurements of viscosity of PVDF solutions in NMP are presented in the paper. These solutions are pseudoplastic at high concentrations of the solution and the presence of PVDF. Viscosity was defined as a function of the shear rate. The PVDF and NMP materials and reagents of the biotechnological class were purchased from the Sigma-Aldrich Chemistry Products catalog. The average molecular weight of PVDF was 534,000.

1.2. Preparation of solutions

To prepare polymer solutions the following features were taken into account: the ability to form stable suspension at the stage of polymer dispersion in the NMP, solubility in the NMP and the viscosity of the resulting solution. To prepare a 10% PVDF solution 10 ml of N-methylpyrrolidone was poured into a vessel at ambient temperature. Then a polymer sample (1 g) was added, left for 24 hours, and after that it was dispersed for an hour. The resulting solution was homogeneous, transparent, and it did not contain undissolved particles. Solutions with concentrations of 0.1, 0.2, 0.4, 1, 2, 3, 5, and 7 wt.% were prepared by the same procedure.

1.3. Rheological measurements

The rheological properties of polymer solutions were studied with the use of Anton Paar MCR 52 rotary rheometer with a plane-plane unit (see Fig. 3). The solution was placed into a gap between two round plates 20 mm in diameter. The width of the gap remained constant and it is equal to 1 mm.

The temperature dependence of viscosity was obtained. Temperature was varied between 15 to 40°C. The relationship between viscosity and shear rate was also established. The shear rate was varied between 1 to 200 s^{-1} at constant temperature of 20°C.

Fig. 3. General view of the Anton Paar MCR 52 rheometer

2. Results and discussion

Fig. 4 shows viscosity of solutions versus shear rate.

It is apparent that the shape of the curves for concentrations less than 7 wt.% is typical for Newtonian fluid, i.e., the viscosity does not depend on the velocity gradient. For concentrations of 7 and 10 wt.% the viscosity decreases with increasing shear rate. This behaviour is typical for non-Newtonian (pseudoplastic) fluids. The rheology of PVDF solutions in dimethyl acetate was studied before [13]. It was shown that the viscosity of the solution practically did not change with an increase in the strain rate (Newtonian behaviour) up to concentrations of 15 wt.%. Thus, the present results are in qualitative agreement with the results obtained before [13].

The rheological behaviour of solutions with concentrations of 7 and 10 % is described by the Power Law model:

$$\mu = k\dot{\gamma}^{n-1},$$

where k is a consistency index (Pa·s^n), $\dot{\gamma}$ is the shear rate (s^{-1}), and n is the flow behaviour index. Consistency indexes for the concentrations of 7 % and 10 % are k =215.1 mPa·s^n and k =1245 mPa·s^n, respectively. Flow indexes for the concentrations of 7 % and 10 % are n =0.966 and n =0.954, respectively.

A similar behaviour of viscosity was observed for suspensions of nanoparticles [11] (see Fig. 5). Like polymer solutions, suspensions are Newtonian fluids at low concentrations of nanoparticles. When concentration of nanoparticles in the suspension increases the non-Newtonian properties emerge. However, unlike the solutions considered above, the rheology of nanosuspensions is not always described by the power-law model. In some cases, yield shear stresses τ_0 occur in nanosuspensions and the rheology is better described by the Herschel-Bulkley model:

$$\mu = (k\dot{\gamma}^n + \tau_0)/\dot{\gamma}\,.$$

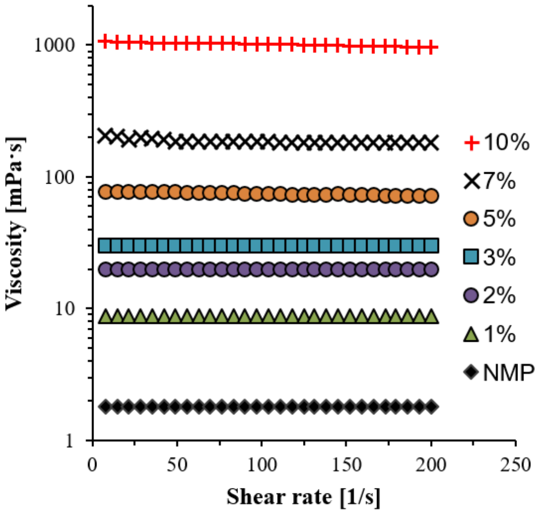

Fig. 4. Viscosity coefficient of the solution versus shear rate at different weight concentrations of PVDF in NMP

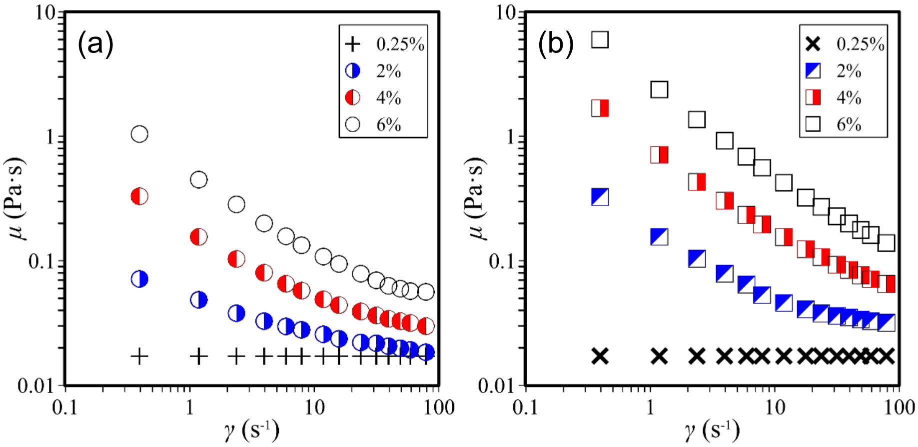

Fig. 5. Viscosity coefficient versus shear rate for ethylene glycol-based nanosuspensions with 150 nm particles of Al_2O_3 (a) and TiO_2 (b) [11]

The volume not occupied by molecules (free volume) is very small in fluids. Then even small molecules from the faster-moving layer can not penetrate the slower-moving layer. As a result, the exchange of the momentum between the layers does not result from the collisions of molecules but because fast-moving molecules entrain the slow-moving molecules.

Polymer molecules are fully oriented and straightened at high shear rates. Then the transfer of momentum from the faster-moving layer to the slower-moving layer should occur in the same way as in fluids since the size of the free volume is small to accommodate a long molecule. Therefore, the viscosity at high shear rates will be low. It approaches the value characteristic for fluids consisting of monomeric rather than polymer molecules [14]. Fig. 6 shows the relationship between the viscosity coefficient and the weight concentration of solutions at three different shear rates (69.6, 131, and 200 s^{-1}). It is apparent that viscosity coefficient does not depend on shear rate. The viscosity coefficient increases with increasing concentration. A deviation from the

Newtonian behaviour begins at concentrations of more than 7 wt.%.

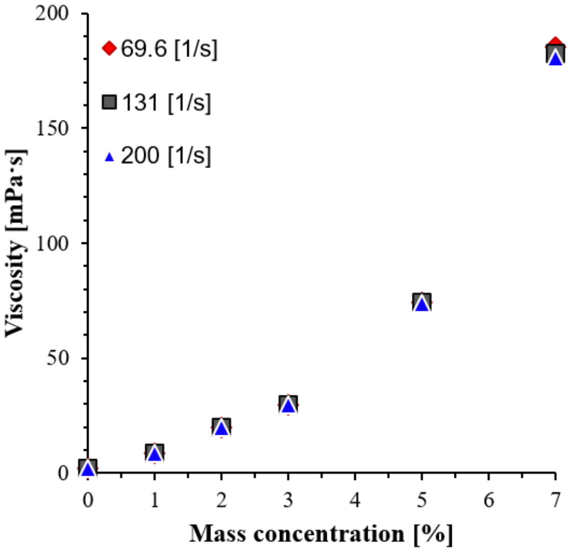

Fig. 6. Relationship between the viscosity coefficient and the weight concentration of solutions at three different shear rates (69.6, 131, and 200 s^{-1})

For solutions with concentrations of up to 7 %, the relative viscosity coefficient was calculated (the viscosity coefficient of the solution referred to the NMP viscosity coefficient). The relationship between the relative viscosity coefficient and concentration is well described by a quadratic correlation (coefficient of determination $R^2 = 0.996$):

$$\mu_{rel}(C) = 1 + a \cdot C + b \cdot C^2,$$

where $a = 2.11$, $b = 1.16$. The relationship between viscosity coefficient of the nanosuspension and particle concentration is generally also nonlinear. For example, the viscosity coefficient of water-based nanofluids with Al_2O_3 (150 nm) particles is described by following equation

$$\mu_{rel}(C) = 1 + 1.52 \cdot C + 4.61 \cdot C^2.$$

Temperature dependences of the viscosity coefficient and relative viscosity coefficient of PVDF solutions in NMP at different weight concentrations are shown in Fig. 7. It was found that the relative viscosity coefficient is independent of temperature:

$$\mu_{rel}(C, t) = \mu_{NMP}(t) \cdot \mu_{rel}(C).$$

At high concentrations (above 7 %) these fluids exhibit non-Newtonian behaviour. Similar phenomenon was observed for suspensions of nanoparticles [12]. So, it was shown that at low concentrations of particles the relative viscosity of nanosuspensions does not depend on temperature.

It should be noted that the viscosity of solutions, like the viscosity of low-molecular fluids, decreases with increasing temperature. This is because the average distances between the molecules increase with the increase of temperature, and the mutual attraction between molecules weakens. For example, the temperature dependences of the viscosity coefficient of PVDF solutions in dimethyl acetate were studied at concentrations above 14 wt.% [15]. Like in the present work, Newtonian behaviour is exhibited by solutions at temperatures up to 30°C while at the temperature of 50°C the phase transition and destruction of the pseudo structure was detected.

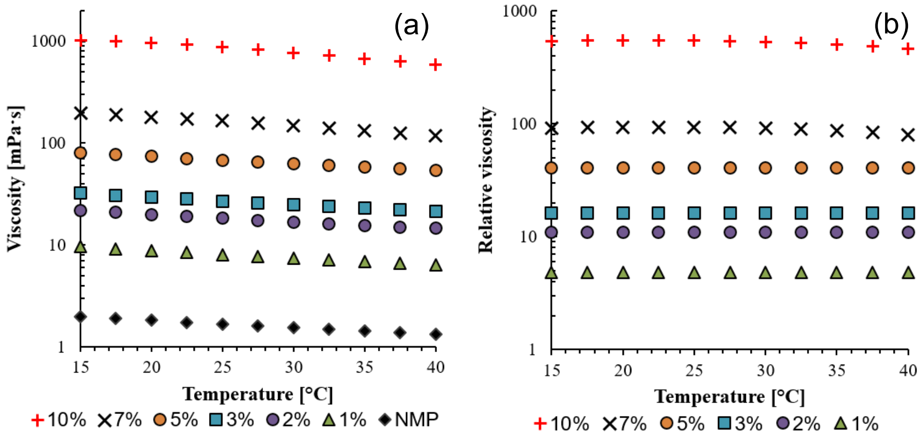

Fig. 7. Relationship between viscosity coefficient (a) and relative viscosity coefficient (b) of PVDF solutions in NMP and temperature at different weight concentrations

Conclusions

The rheological properties of PVDF solutions in N-methylpyrrolidone were studied. It was shown that the viscosity coefficient of polymer solutions decreases with increasing temperature though this relation ship is not linear. The viscosity coefficient of the pure N-methylpyrrolidone solution remains almost constant. As shown experimentally, solutions with concentrations of PVDF up to 7 wt.% behave as Newtonian fluids, i.e., their viscosity does not depend on shear rate. For higher concentrations of PVDF, the pseudoplastic behaviour was observed. It was demonstrated that addition of polymers allows one to modify the behaviour of solutions.

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Реологические свойства растворов ПВДФ

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Аннотация. Реологические свойства растворов ПВДФ в н-метилпирролидоне исследованы реометрическим методом. Было показано, что вязкость растворов полимеров нелинейно уменьшается с увеличением температуры. Вязкость растворителя — н-метилпирролидона — остается практически неизменной. Показано, что при массовых концентрациях менее 7 % растворы проявляют ньютоновское поведение. При более высоких концентрациях растворы проявляют псевдопластические свойства.

Ключевые слова: жидкости, структура, вязкость, реологические свойства, ньютоновское и неньютоновское поведение, полиминилденфторид (ПВДФ), н-метилпирролидон, свойства материалов, температурные зависимости.