

Effects of Polymeric Additives on Thermal Ink Jets

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Abstract

The work was undertaken to study the ability of small amounts of polymeric additives to the ink to suppress the disintegration of the ink jet in flight and consequently to remove the sputter. To estimate the appropriate range of the polymer parameters the possible effects of polymeric additives on different stages of thermal jet printing were theoretically analyzed. The low concentration solutions of polyacrylamide in the standard ink and in the model solvent were used in the experimental investigations. The jet of the standard ink is disintegrated in two stages: at the first stage the thin neck between the head drop and the long tail is broken and then the tail is disintegrated into a number of small secondary droplets. Polymeric additives cardinaly modify this process. The neck between the head drop and the tail is stable for all investigated polymeric fluids. Depending on molecular parameters (molecular mass and concentration) four cases are possible. The first one is when the tail is simultaneously disintegrated along its axis into a number of small droplets. The second case is when the end of the long tail is disintegrated into a few secondary droplets whereas the main part of the tail is drawn into the prime drop. The third case is when the whole tail is drawn into the head drop without any losses of liquid and the single drop is thus formed. Finally, the fourth case is when the expelled drop is returned into the nozzle wall under the action of inner elastic stresses in the tail. It was shown experimentally that the polymeric additives used do not affect the flow in the printhead chamber as well as the sizes of dots on the paper and printhead lifetime.

Introduction

Wide employment of polymeric additives in different branches of industry is caused by their ability to essentially change the character of the flow. The most remarkable property of polymer additives to suppress the disintegration of the fluid is attractive for the jet printing because the flight instability and the breakup of the expelled ink jet lead to the decrease of the printing quality. On the other hand, it is known that polymeric agents are used to improve the adhesive properties of the ink if printing is not on paper, but on smooth surface. Moreover, polymeric additives are included into the composition of the dye in the application of jet printing to textiles.

Effects of polymeric additives

Before studying the influence of polymeric additives on the process of thermal ink jet printing it is necessary to choose the group of polymeric additives which may be suitable for this process. We intended to modify the droplet in-flight disintegration whereas not to affect any other process elementary stages. The following theoretical estimates constitute the basis of searching for the polymeric additives that satisfy these requirements.

It is commonly accepted that anomalous hydrodynamic effects in polymer solutions are caused by the formation of additional inner elastic stresses in high-strain extensional stages of flow. It is assumed that in the strong extensional flow coiled flexible polymer molecules become considerably extended, their hydrodynamic interaction leads to high resistance to flow, and consequently liquid elasticity appears. The crude model (Oldroyd-B) considers just the gross deformation by the flow of coiled polymer [1]:

$$\underline{\underline{\sigma}} = -p\underline{\underline{I}} + 2\mu\underline{\underline{E}} + G(\underline{\underline{A}} - \underline{\underline{I}}) \quad (1)$$

$$D\underline{\underline{A}}/Dt = \underline{\underline{A}} \cdot \nabla \underline{\underline{v}} + \nabla \underline{\underline{v}}^T \cdot \underline{\underline{A}} - (\underline{\underline{A}} - \underline{\underline{I}})/\theta \quad (2)$$

where $\underline{\underline{\sigma}}$ is the stress tensor, p is the pressure, μ is the shear viscosity, G is the elasticity modulus, $\underline{\underline{E}}$ is the strain rate tensor, $\underline{\underline{A}}$ is the elasticity deformation tensor, $\underline{\underline{I}}$ is the unit tensor, t is the time, $\nabla \underline{\underline{v}}$ is the velocity gradient, θ is the relaxation time. For dilute polymer rheological constants G and θ of Oldroyd model are usually taken to be [1] $G = 3nkT$, $\theta = 2\pi\mu z_0^3 / (kT)$, in which kT is the Boltzmann temperature, n is the number density of the polymers, z_0 is the equilibrium size of coiled macromolecule. Consequently, $G \propto c/M$, $\theta \propto M^{3/2}$ (c - polymer concentration in solution, M - molecular mass of polymer). Thus, by appropriate choice of molecular mass and concentration it is possible to obtain any desirable values of elasticity modulus and relaxation time. The parameters G and θ can also be determined experimentally [2, 3]

The influence of polymeric additives on the following stages of thermal jet printing were considered: vapor bubble growth and collapse, formation of the ink jet, disintegration of the jet in the flight, impact of a droplet on the paper. It was assumed that the geometry of elementary printhead chamber corresponds to the standard Hewlett-Packard printhead. All stages include the axial or plane extension of the liquid. The forming elastic stresses can modify the processes discussed here. All estimates are based on Eqs. (1)-(2).

The effect of additional elastic stresses in the process of bubble growth is undesirable because they inhibit the bubble growth. If the formed elastic stresses are much less than the inertial forces in the liquid, then the influence of elasticity will be negligible. It takes place if

$$G \ll \rho v^2 (a/D_c)^2, \quad (3)$$

where ρ is the liquid density, v is the typical velocity of jet, a is the lateral size of thermal ink-jet heater, D_c is the lateral size of elementary printhead chamber.

It also follows from the theory that the polymeric additives reduce the bubble collapse at the final stage:

$$R \geq \frac{GR_0 \exp(-t/\theta)}{(2/3)(p_\infty - p_v) + 2\alpha/R_0}, \quad R \ll R_0, \quad (4)$$

where R is the current bubble radius, $R_0 \approx D_c$ is the maximum radius of the vapor bubble, p_∞ is the pressure far away from the bubble, p_v is the pressure inside bubble, α

is the surface tension. This slowing-down will prevent the formation of high intensity shock waves in the fluid that cause the damage of thermoresistor.

When the bubble is growing the jet is forming. The flow near the exit is convergent and consequently the fluid elements are subject to the extension in the direction of the flow. The formation of elastic stresses in the convergent flow and their influence on the dynamic of the ejection were studied by Bazilevsky et al. [4] and Entov et al. [5]. The influence of polymer on jet formation will be negligible if

$$G \ll \rho v^2 \left(\frac{d}{D_c}\right)^4 \exp\left(\frac{D_c}{v\theta}\right), \quad (5)$$

where d is the diameter of the nozzle orifice.

Droplet breakoff takes place when bubble growth is ceased. It is the most critical stage of printing process for formation of the sputter. The expelled jet consists of a relatively large head (prime drop) and thinning long tail [6]. The cylindrical liquid volume is unstable due to the action of capillary forces and tends to breakup into droplets. For the inviscous fluid (the case of standard ink) the breakup time is defined by the balance of capillary and inertial forces and is of the order of $t_\rho \approx (\rho d^3 / \alpha)^{1/2}$. It was shown [4] that axial elastic stresses in the polymeric jet prevent it from disintegration. The jet is stable until the axial elastic stress is larger than the capillary pressure in the jet. The characteristic breakup time of the jet of polymer solution is of the order of the relaxation time: $t_\theta \approx \theta$. Therefore the polymer additives can stabilize the jet if

$$t_\theta \approx \theta \geq t_\rho \approx (\rho d^3 / \alpha)^{1/2} \quad (6)$$

Elastic stresses arising in the fluid in the course of the process of the drop breakoff slow down the motion of the prime drop and consequently lead to a loss in the velocity of the drop. Estimates show that if

$$v \gg G\theta D_c^4 / (\rho d^5) + \theta\alpha / (\rho d^2) \quad (7)$$

then the velocity loss is negligible. When inequality (7) is invalid the drop is unable to come off the nozzle and the printing process is impossible.

The viscous friction is a dominant factor in the process of the collision of the ink drop with the paper. The effect of elasticity will be negligible if

$$Eu \gg 2(1 + 2\text{Re})^{2/5} - 2, \quad (8)$$

where $\text{Re} = \rho v d / \mu$, $Eu = \rho v^2 / G$

Estimates (3)-(8) allow us to choose the polymer and the molecular parameters M and c that are appropriate for

the above mentioned goals. In numerical estimates we have used the parameters which approximately corresponded to the standard HP ThinkJet printhead. It was concluded that the most preferable polymer is polyacrylamide (PAM, $[-CH_2 - C_2ONH_3 -]_n$) with molecular weight from a few hundred thousand to several million. It is well-soluble in water, glycerin, alcohol etc., i.e. in the fluids which may be included in the thermal ink. PAM solution is non-aggressive, non-toxic, time and temperature stable enough. For PAM of molecular mass $M=500,000 - 6,000,000$ the relaxation time θ changes in the range of 0.0047 - 0.025 sec and ratio of elastic modulus G and weight/weight concentration c changes in the range 150,000 - 12,000 dyne/cm². Hence, the available polymers cover wide range of rheological parameters G and θ .

Experimental

Model liquids for the experiments were prepared as follows. First, 1% solution of polyacrylamide was prepared by dissolving the polymer powder in distilled water during long time (one week). Just before (about one hour) the experiments this solution was diluted to 0.1% concentration and then it was added to a water-glycerin mixture (50/50) to obtain a desirable concentration of polymer. The liquids were used once and only during short period (1-2 days) to rule out the possibility of polymer degradation processes.

The water-glycerin mixture was used as a model for the standard ink. The viscosity of the mixture is approximately the same as the viscosity of the standard ink - 5 cP.

Steady shear viscosity measurements were performed in coaxial cylinder viscometer at shear rate range of 25–1300 s^{-1} . It was observed that the shear viscosity of PAM solutions is considerably higher than that of pure solvent only at low shear rates. For the ink jet formation process high shear rates are typical. They can be estimated to be about $10^5 s^{-1}$. Therefore the shear viscosity of the used PAM solutions may be considered equal to the viscosity of the solvent.

The experimental set up for visualization of jet formation was used in the investigations. It allowed to visualize the process of droplet ejection within few millimeters from the nozzle and monitor different stages of the ejection. The frame sequences were saved on the video tape and then in the PC as graph files for further analysis. All experiments were carried out with jet cartridges of the ThinkJet model. When investigating polymer solutions, the disassembled printheads fed from the external reservoir were used.

Results and discussion

Sequence of frames depicting the jet generation

All possible combinations of the following parameters were investigated: Molecular mass $M = 500,000; 2,000,000; 6,000,000$. Polymer concentration $c = 0, 10, 25, 50, 100, 200$ p.p.m. Standard ink and water-glycerin mixture were used as solvents. Operating dot frequency $f = 50, 1000$ Hz. Standard firing conditions were used.

It was experimentally observed that the process does not depend on the operating frequency ($f = 50$ or 1000 Hz) for all investigated fluids. It was observed also that the influence of the kind of the solvent (standard ink or water-glycerin mixture) is not significant. The last statement allows to consider the water-glycerin mixture as a hydrodynamic model of standard ink.

The most typical situations are presented on the figures 1-5. The states of a drop correspond to different moments of time after firing. In all cases the longitudinal size of the frame corresponds to 2.21 mm on real scale.

The figure 1 shows the process of the ejection of a drop of HP standard ink. A long tail is formed. The neck between the prime drop and the tail breaks up approximately 80 microseconds after firing and the tail loses a contact with the prime drop. Then during approximately 150 microseconds after firing the tail disintegrates simultaneously along its axes into a number of the small secondary droplets. As a result the prime drop is accompanied by an extended cloud of secondary droplets.

The figure 2 demonstrates the ejection of a drop of PAM solution of concentration $c=50$ p.p.m. and molecular mass of $M=500,000$. The prime drop and the very long tail are formed. There is no two stage disintegration as in the case of the ink and the water-glycerin model fluid. The neck between the prime drop and the tail is stable up to the moment of tail disintegration. Tail is disintegrated along its axis simultaneously in approximately 400 microseconds after firing. Similar behavior of the jet takes place for concentrations $c=10$ p.p.m. and 25 p.p.m. of the same polymer ($M=500,000$). Probably we have the situation that corresponds to exceeding of elastic stress under capillary pressure in the jet. These high elastic stresses inhibit the disintegration of the tail into the secondary droplets up to a moment of relaxation of elastic stresses to a capillary pressure level (about of 400 microseconds). The formation of a very long tail may be explained by the mechanism discussed in [5]: Due to low molecular mass the elasticity modulus has a large value. Consequently, the high level of elastic stress is formed. High elastic stresses in the jet stretch out the fluid from the nozzle after cessation of vapor bubble growth (the ejection of the fluid from the nozzle is lasted about 300 microseconds !). To classify the possible types of drop ejection we shall name the case of tail disintegration simultaneously along its axis as a case

number One. This behavior is typical for low molecular mass and small or intermediate concentrations as well as for very small concentrations independently of molecular mass. However in the last situation the tail is not so long.

The PAM solution of $M=2,000,000$, $c=25$ p.p.m. demonstrates another type of in-flight disintegration: a case number Two. Under the action of capillary and elastic stresses the tail is drawn into the prime drop. A few secondary droplets are detached from the tail end. Then these secondary drops continue independent flight or unite with the prime drop.

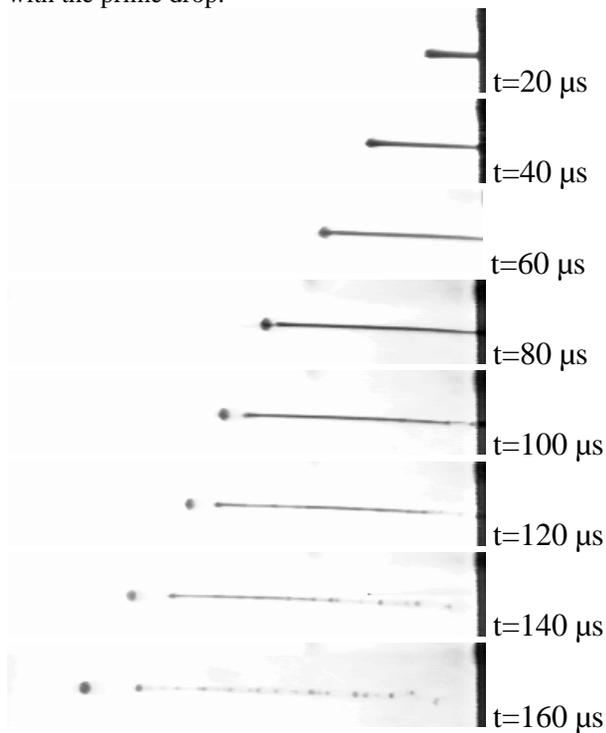


Figure 1. Ejection of jet standard ink.

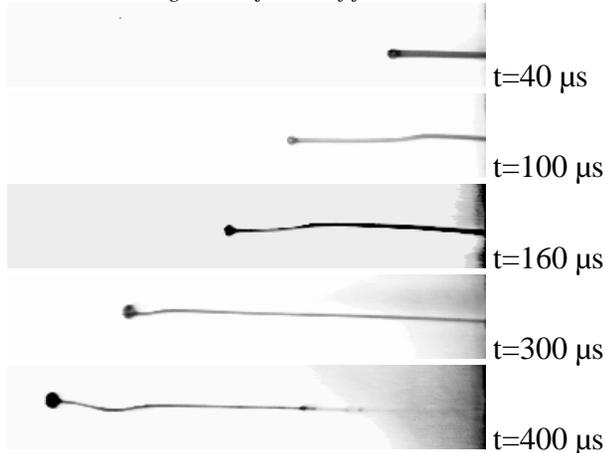


Figure 2. Ejection of jet of PAM solution, $c=50$ p.p.m., $M=500,000$.

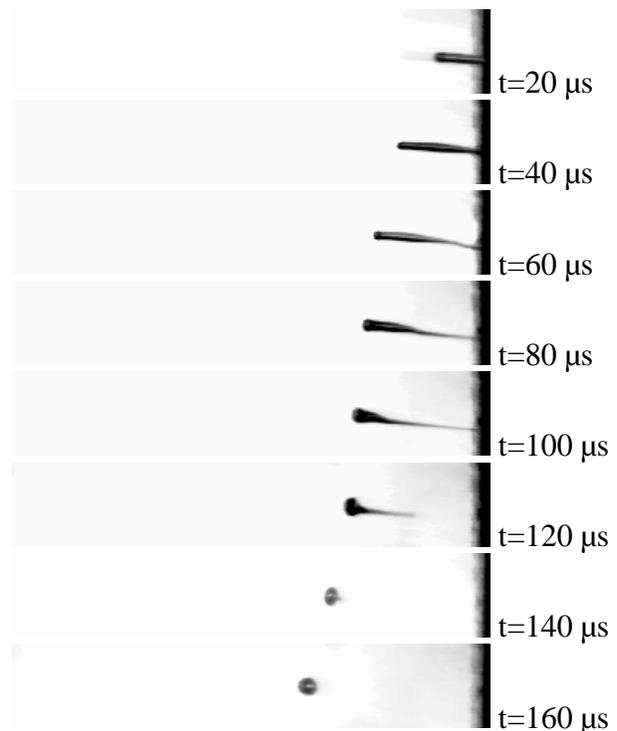


Figure 3. Ejection of jet of PAM solution, $c=100$ p.p.m., $M=2,000,000$.

Formation of a single drop (case number Three) is demonstrated on Figure 3. The tail is drawn into the prime drop without the formation of secondary droplets. This type of ejection is typical for intermediate concentrations and high molecular masses.

The process of return of the ejected drop to a nozzle was observed for high polymer concentrations (case number Four). The elastic stresses in the tail retard the prime drop forcing the reverse motion (see estimate (7)). All high concentrated polymer solutions display similar behavior.

Figure 4 shows the type of the ejection as a function of molecular parameters. It should be noted that there are no sharp boundaries between these cases, hence, the Figure 6 displays only qualitative tendencies.

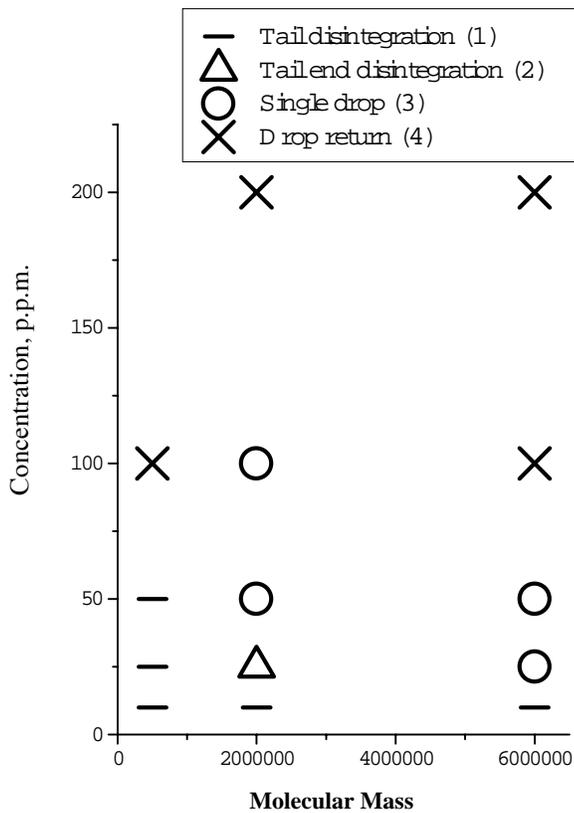


Figure 4. Influence of molecular parameters upon type of ejection.

Drop displacement

To estimate the influence of molecular (molecular mass and concentration) and other parameters on the values of drop velocity losses the measurements of displacement of drop head versus time were carried out. The drop displacement is a distance between the nozzle surface and the head of the drop. The typical graphs are presented on the Figure 5. The curves allow to determine the drop flight velocity in each case. The conditions of the experiment are presented in the figures. The note “#2” means that in addition to one measurement the experiment with another nozzle was carried out.

The results display that the polymeric additives have no influence on the ejection process in the course of the first 50 microseconds. It means that the polymer does not influence the bubble growth and the flow in the chamber. The graphs show the influence of molecular parameters on velocity losses. Experimental data qualitatively coincide with the theoretical predictions.

The results of the measurements of the drop displacement showed also that the dot frequency has no influence on the velocity of the drop of polymeric fluids. Similarity of the results obtained for PAM solution in water-glycerin mixture and in the standard ink displays that there is no chemical counteraction between polymer and ink content.

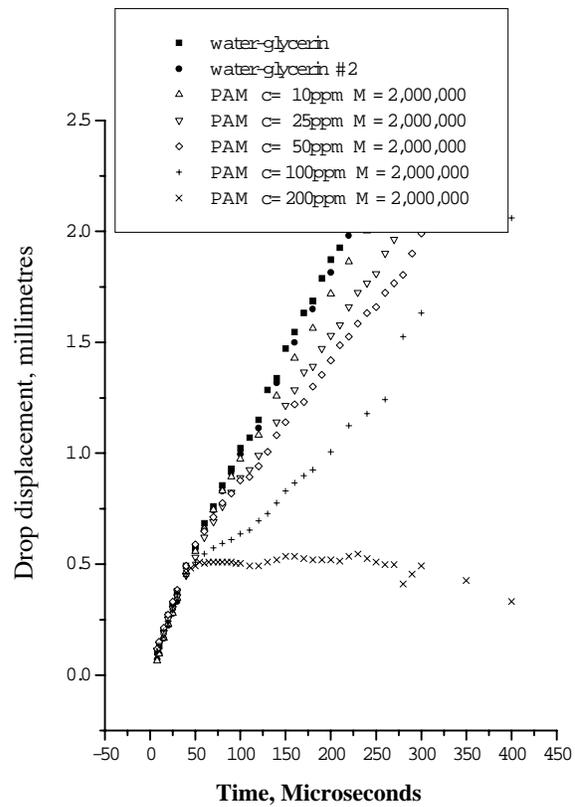


Figure 5. Flight displacement of drop PAM solution ($M=2,000,000$).

It should be mentioned that we monitored the drop head displacement. It is likely that the values of the velocity loss are less if the motion of center of mass is taken into account: while the drops of ink are extremely extended objects, the polymeric droplets are compact objects..

Dimensionless constitutive parameters

We used the ThinkJet printhead in present investigations to understand the general fundamental conformities to natural laws of influence of polymeric additives on printing process. It seems that the transformation of obtained results in the case of other linear scales may be made in following way. Indeed, the influence of polymers is reduced to the counteraction of arising additional elastic forces and the surface forces that tend to disintegrate the liquid object (drop). Thus, to ensure the similarity of the two cases where ejected droplets differ in linear sizes it is necessary to keep the same correlation between elastic and surface forces in both cases. Surface pressure is of the order of α / d (α -surface tension, d -jet diameter), elastic stress is proportional to the fluid elasticity modulus G and the square of the fluid extension ratio. Supposing that the extensions of the fluid are the same in both cases we conclude that to keep the same correlation between elastic and surface forces it is necessary to keep the same dimensionless constitutive parameter $A_1 = Gd / \alpha$.

Another dimensionless constitutive parameter follows from the necessity of similarity of time change of the elastic stress level and time evolution of the jet (break off, disintegration, etc.). As it was noted earlier the characteristic time of the jet evolution is of the order of $t_1 = (\rho d^3 / \alpha)^{1/2}$. The characteristic time of the stress change is the fluid relaxation time θ . Hence the second dimensionless constitutive parameter is $A_2 = \theta / (\rho d^3 / \alpha)^{1/2}$.

Constancy of parameters A_1 , A_2 defines the condition of similarity. In particular if the diameter of the nozzle is decreased (droplet volume is decreased) the elasticity modulus should be increased by the same factor ($A_1 = \text{Const}$) and relaxation time should be decreased in accordance to the requirements of constancy of parameter A_2 .

Dot formation. Print quality

The measurements of the sizes of the dots on paper and transparency film showed that there is no difference between the standard ink and the polymer solution of the same viscosity. Lifetime testing carried out on the limited number of printheads showed that the polymeric additives do not reduce the lifetime of printhead.

Conclusions

1. The polymeric additives can modify the jet generation. It is possible to observe the following cases of the ink jet disintegration: simultaneous disintegration of the drop tail into a number of small secondary droplets; disintegration of the end of the tail into a few secondary droplets and drawing of the rest of the tail into the prime drop; compression of primary extended drop into compact drop without any loss of continuity; return of the ejected drop into the nozzle under the action of elastic stresses in the drop tail. The desired positive effects on printing process may be achieved by a proper choice of rheological parameters, which can be controlled by the molecular mass and the concentration of the polymer.

2. The positive effects of polymeric additives on the jet disintegration process can be achieved without the variance in all other printing processes stages.

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