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Influence of Surface Energy of Polymer Films on Spreading and Adhesion of UV-Flexo Inks

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Abstract:

Most technological processes involved in polygraphic production are based on the interaction between liquids and solids. An important role is thereby attributed to the wetting phenomenon which ensures ink transfer and adhesion of printing inks, primers, varnishes to the surface of substrates. The interaction between ink and solids in the printing process provides intermolecular interaction in both, the liquid (cohesion) and the liquid with solids phases (adhesion). This research studies the influence of surface energy of polymeric films and polarity on spreading and adhesion of flexographic UV-inks.

Keywords:

Polymer Films, UV-Inks, Surface Energy, Adhesion, Viscosity, Contact Angle

1. Introduction

Polymer film materials are used to print labels and packaging by means of flexography. It is known that the surface of polyolefins such as polyethylene, polypropylene, etc., has low surface energy because there is a lack of molecular interactions between polymer surfaces and inks, and as a result images with low optical characteristics are created. In the worst case, a layer of ink may be flaking. Nowadays, the most common method of increasing the surface energy of polymer films is the activation by primers *(Cushing; Repeta et al., 2008*) and corona treatment *(Markgraf; Mesic, Lestelius, 2005; Repeta et al., 2003*). In the case of corona treatment of polymer films, the given level of surface energy eventually starts to decrease and becomes close to the original *(Lukin, 2002)*.

Good surface wettability is a prerequisite for ensuring good adhesive bonding. Wettability is defined by the contact angle of the liquid with the solid phase. The surface contact angle that arises when a liquid is placed on a solid surface can be analyzed in terms of thermodynamic equilibrium. The equation describing this equilibrium can be expressed as:

$$\gamma_L \cdot \cos\theta = \gamma_S - \gamma_{SL} \qquad (1)$$

which is known as Young's equation, where γ_{SL}, γ_L, and γ_S are the interfacial tensions between the solid and the liquid, the liquid and the gas, and the solid and the gas, respectively.

The relationship describing the adhesion work between the solid and the liquid can be expressed as:

$$W = \gamma_L (1 + \cos\theta) \qquad (2)$$

which is known as Dupre equation.

Dupre equation shows that the improvement of the spreading liquid (cosine of the contact angle increases), the work of adhesion is increases. According to Young and Dupre equations the adhesion is good with high surface energy of solids.

In recent years there has been a tendency to implement UV- technology in flexographic printing. UV-printing is different from conventional printing in many ways. As UV-inks harden in a split second using UV-radiation in the printing press, the prints can be instantly forwarded to post press operations and film thickness shows high resistance to mechanical influences such as scraping and scratching. UV-flexo inks have a higher viscosity than solvent-based inks and thus require high surface energy of polymer films.

The aim of this research is to study the impact of surface energy and polarity of polymer films on the spreading and adhesion of flexographic UV-inks.

2. Methods and Materials

OPP films VLD type (Treofan Group) with different storage time from the date of manufacture were selected for this study. Flexographic UV-inks Deltaflexo (Colorgraf S.p.A., Italia) were also used. For the contact angle measuring polymer films is divided into parts. In our case, the sample size of 100 × 100 mm was conventionally divided into 25 squares. In each square there was a drop of liquid. The cosine of the contact angle was calculated by the height and diameter of liquid drop deposited on the polymer film, by means of this formula:

$$\cos\theta = [(d/2)^2 - h^2] / [(d/2)^2 + h^2] \qquad (3)$$

where d is the diameter of the base of the drop placed on the film and h is the height of the drops over the surface of the film

Drop images were captured with a CCD camera (1280×720 px) attached to the microscope, and then recorded by computer. Small test liquids and ink droplet 7.5±0.5 μl is placed on the substrate with a micropipette. The spreading of the test liquids and UV-inks was evaluated in 1 min. after application on the substrate out at temperature 20±0.5 °C and 80 % relative humidity.

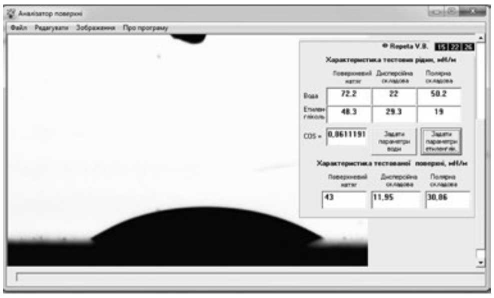
Polar and dispersion components of surface energy for wetting angle of test liquids (distilled water and pure ethylene glycol) are determined by Owens-Wendt-Rabel-Kaelble method (OWRK) *(Owens, Wendt, 1969):*

$$0.5\gamma(1+\cos\theta)/(\gamma_d)^{0.5} = (\gamma_d^{\,s})^{0.5} + (\gamma_p^{\,s})^{0.5}(\gamma_p/\gamma_d)^{0.5} \qquad (4)$$

where: γ – surface tension of the liquid, γ_d and γ_p – dispersion and polar components of the surface energy, that characterize solid body S or liquid (index missing).

For the calculation of this connection, which lies in the coordinates $0.5\gamma(1+\cos\theta)/(\gamma_d)^{0.5}$ - $(\gamma_p/\gamma_d)^{0.5}$ is a straight line with a slope of $(\gamma_p^{\,s})^{0.5}$, and the point of intersection of this line with the axis of ordinates – $(\gamma_d^{\,s})^{0.5}$, was used the developed program, which interface is shown in Fig. 1.

A calculation of the surface energy of films, which used the Elton equation *(Mitchell, Elton, et al., 1953)*, was conducted to compare the results. Taking into account that the result of calculation by means of this equation depends



Характеристика тестових рідин, мН/м

	Поверхневий натяг	Дисперсійна складова	Полярна складова
Вода	72.2	22	50.2
Етилен гліколь	48.3	29.3	19

cos = 0,8611191

Характеристика тестованої поверхні, мН/м

Поверхневий натяг	Дисперсійна складова	Полярна складова
43	11,95	30,86

Figure 1. Interface of the program for determining wetting angles, polar and dispersion components by OWRK method.

on the nature of the test fluid (drawback of this method), ethylene glycol and dimethyl sulfoxide were used and the face value of the surface energy was taken from the average value of the two results of testing:

$$\gamma^1_s = 0.5\,(\gamma^{et}_{lv} + (\gamma^{et}_{lv} \cdot \cos\theta))$$

$$\gamma^2_s = 0.5\,(\gamma^{d}_{lv} + (\gamma^{d}_{lv} \cdot \cos\theta)) \qquad (5)$$

$$\gamma^E_s = (\gamma^1_s + \gamma^2_s)/2$$

where: γ^{et}_{lv} – surface tension of ethylene glycol;
γ^{d}_{lv} – surface tension of dimethyl sulfoxide;
γ^1_s – surface energy of the film during the testing of ethylene glycol;
γ^2_s – surface energy of the film during the testing of dimethyl sulfoxide;
cos θ – cosine of the contact angle of appropriate test-fluid wetting.

Table 1 provides the characteristic of test liquids.

Viscosity of flexographic UV-inks was determined with the Brookfield RVT viscometer, rotor № 7, temperature 15 °C. Tape peel adhesion testing (Scotch-test) was conducted according to ASTM F2252-03 using the Scottish Magic tape (3M).

3. Results and discussion

The adhesion of ink compositions to the substrates depends on intermolecular interactions between them. It can be expressed as the sum of works of adhesion for different types of interactions (polar γ^r and dispersive γ^d), giving as a result the overall thermodynamic work of adhesion of boundary division solid-liquid. Table 2 provides the results of determining of the surface energy of polymer films and its components.

As visible in table 2, the determination of surface energy by two methods gives approximately the same result, but the Owens-Wendt method allows a more accurate assessment of energetic properties of polymer films. Selected films have different surface energy, which indicates the changes that occur in the upper layer

Table 1. The test liquids used and their properties

Test liquids	Surface tension, mJ/m^2		
	Total, γ	Disperse, γ_d	Polar, γ_p
Distilled water	72.2	22	50.2
Ethylene glycol (Dow Chemical)	48.3	29.3	19
Dimethyl sulfoxide (Gaylord Chemical)	43.6	34.9	8.7

Table 2. Energy characteristics of the surface of studied films

Polymer films	Surface energy (OWRK method)			Polarity, γ_p/γ_s	Surface energy γ^E_s, mJ/m^2 (Elton method)
	Polar component γ_p, mJ/m^2	Dispersion component γ_d, mJ/m^2	Surface energy γ_s, mJ/m^2		
PP1	25.6	13.9	40.4	0.63	38.5
PP2	32.5	14.2	46.7	0.69	43.9
PP3	23.8	14.5	38.3	0.62	37.4
PP4	18.6	12.8	31.4	0.59	34.4

of films during storage. In this case the change relates to the polar component of surface energy, because the dispersion component does not change. Decontamination of polar groups leads to reduced polarity so the polarity of PP2 film is 0.69 and the polarity of the PP4 film 0.59. Fig. 2 displays the difference in the polarity of the film surface.

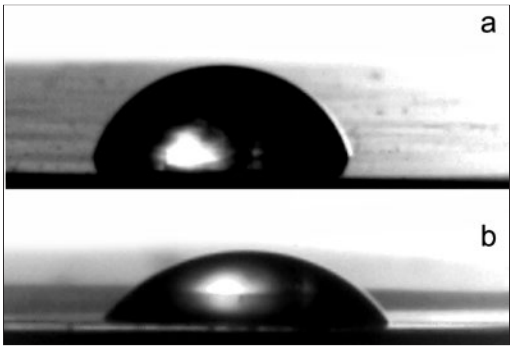


Figure 2. Spreading of distilled water on the PP4 film surface. (surface energy 31.4 mJ/m^2, polarity 0.59) (a), spreading of distilled water on the PP2 film surface (surface energy 46.7 mJ/m^2, polarity 0.69) (b).

For the research of the influence of surface energy on spreading UV-inks inks with a series of different pigments were taken: yellow – azo-pigment, cyan – copper phthalocyanine, black – carbon.

As shown in Fig. 3, with the increase of surface energy of films, the spreading of inks increases, similarly as in the case of distilled water. It is clear that the driving factor here is the polar component of surface energy. The figure also shows that yellow inks spread the best and the black the worst. This can be explained by the differing ability components of the ink to the structure formation (thixotropy), a phenomenon that leads to increase of viscosity and reduced spreading of drops of ink due to the bonds between the components of the ink. Thixotropy can be characterized by the viscosity anomaly. It is known that phthalocyanine pigments, especially carbon, can provide inks with thixotropic properties, as is visible in the results of viscosity abnormalities of inks studied (Tabl. 3). Blue and black inks have viscosity anomaly of 1.4 and 1.7, which is more than yellow ink viscosity anomalies (1.28) and as a result – the reducing of spreading rate.

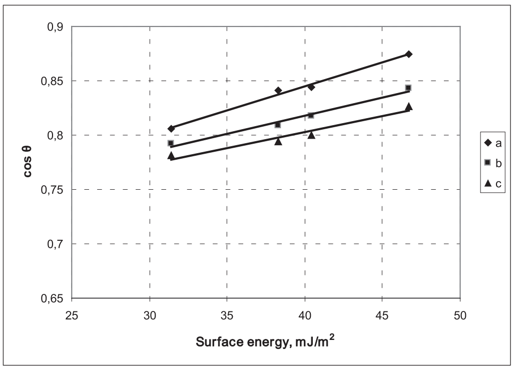


Figure 3. The influence of values of surface energy of films for spreading Yello UV-inks (a), Cyan UV-inks (b), Black UV-inks (c).

Table 3. Anomaly of viscosity of UV-inks Deltaflexo

UV-inks	Viscosity max., Pa·s	Viscosity min., Pa·s	Anomaly of viscosity
Yellow	7.2	5.6	1.285
Cyan	8.0	5.6	1.428
Black	9.6	5.6	1.714

As mentioned above, the spreading value is a prerequisite for adhesion of the printing ink to the film, so we conducted a Scotch-test to determine the adhesion of UV-inks. Visually the difference in adhesion parameters is shown in Fig. 4. As seen from the figure, the adhesion of UV-ink to the film PP2 is the maximum (a), and in the case of polypropylene film PP4 complete exfoliation is observed (b).

In the case of PP1 and PP3 films partial exfoliation of paint layer was observed, with marked heterogeneity of adhesive interactions in the film plane.

4. Conclusion

Studies have shown that the maximum spreading and maximum adhesion of UV-inks is possible at high surface energy and polar component of the surface film. That characteristic has particular film PP2 with surface energy 46.7 mJ/m^2 and polar part of the 32.5 mJ/m^2. For example, it provides good spreadability of

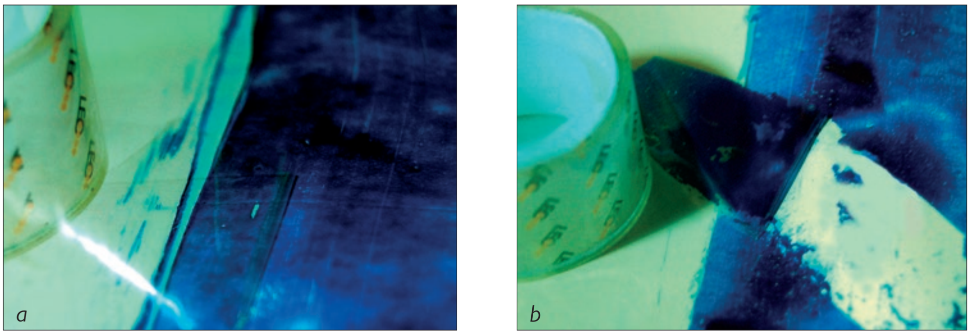


Figure 4. Scotch-test ink layer on the film surface PP2 (a), scotch-test ink layer on the film surface PP4 (b).

UV-inks with different ability to structure formation. In the above-mentioned surface energy and polar component cosine contact angle UV-inks Cyan is 0.843. In the case of film PP4, whose energy and polar component is respectively 31.4 and 18.6 mJ/m^2, the cosine of the contact angle is 0.792. According to Dupre equation, decreasing cosine of the contact angle causes to reduces of ink adhesion. The polarity of the surface shows the presence of polar groups in intermolecular interactions provide an adequate adhesive bond. As a result of Scotch-test we see reduced adhesion of ink layer on the film surface PP4 whose polarity is 0.59 and the polarity of the film PP2 - 0.69 ensured good adhesion.

There is also a small difference in spreading inks with different types of pigments. This can be explained by the differing ability components of the ink to the structure formation (thixotropy), a phenomenon that leads to increased viscosity that reduced the spreading of drops of ink. Accordingly, a drop of black ink over other inks has a lower capacity for spreading and requires more time to reach equilibrium. It is characterized by high anomaly of viscosity – 1.7, compared to the anomaly of viscosity for the blue ink –1.4 and for the yellow ink – 1.2.

It is worth noting that even at high values of the surface energy of the film, its wetting by UV-inks is limited, i.e. cohesion of UV-inks exceeds adhesion, thus indicating the high surface tension of printing inks.

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