ANALYSIS OF THE INTERACTIONS IN THE "VARNISH – PHOTOPOLYMER" SYSTEM

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Abstract: Varnishing of the printed product is often carried out by means of a photopolymer flexographic printing plate. Various types of varnishes interacting with a photopolymer material can cause chemical changes in its surface layer and affect the acceptance and transfer of varnish to the print. The aim of this paper is to describe the interactions of different types of varnishes and standard styrene-isoprene-styrene flexographic printing plate and to analyse the influence of varnishes on the surface layer of the photopolymer material. Types of varnishes used in this research are matt and gloss water-dispersive varnish, oil-based and UV varnish. Their interactions with the printing plate were analysed using different methods: contact angles of the varnishes on the printing plate were measured, and surface free energy of the printing plate were carried out in order to assess the effect of the varnishes on the chemical changes in the photopolymer material. Microscopic images of the photopolymer exposed to varnishes and FTIR-ATR spectra were obtained in order to capture visible changes on the printing plate's surface. The results of the research will allow for an assessment of the suitability of a specific type of varnish for flexographic printing.

Key words: photopolymer, varnish, swelling, contact angle, surface free energy

1. BACKGROUND

Flexography is a relief printing technique that uses rotary actions to transfer ink from photopolymer printing plate onto substrate. Flexography developed from the use for low quality images, to a method of wide implementation in printing - from newspaper, packaging to books with capability of using the wide range of printing substrates.

The printing process is simpler than the offset printing and it's the only letterpress process that is in wide use. The main feature is the soft photopolymer flexible printing plate and low viscosity ink, so it makes it possible to print on substrates of different surface properties and roughness, both absorbent and non-absorbent (Brajnović, 2011).

Flexographic inks have very similar viscosity to gravure inks (0,05-0,5 Pas). Flexographic inks are transferred onto the printing plate by the inking unit with a usage of the anilox roller. The viscosity is very important because it influences the ink and varnish properties, with the requirements such as squeezing of the ink or varnish out of the anilox cells (Havlínová et al, 1999).

The solvents used in flexographic printing most often are ethyl acetate, isopropyl alcohol and water. They are used as a component of the inks or as the cleaning agent for the printing plate. Varnishing is often conducted by photopolymer flexographic printing plate. Different types of varnishes interact differently with the photopolymer material. As well as the inks, varnishes can cause physical and chemical changes in the surface of the photopolymer material, which can lead to mechanical issues and low print quality (Tomašegović, 2016). Most common types of varnishes were used in this research: matt and gloss water-dispersive varnish, oil-based and UV varnish.

In this research, experiments of the swelling of printing plate were carried out in order to assess the effect of the varnishes on the chemical changes in the photopolymer material. Contact angles of the varnishes on the printing plate and surface free energy of the photopolymer material were calculated. Microscopic images of the photopolymer exposed to varnishes were obtained in order to capture visible changes on the printing plate's surface that would affect the quality of image reproduction.

The aim of this experimental work was to analyse the influence of different varnishes on the surface of the photopolymer printing plate in order to assess its suitability for the use with the specific varnish. This research enabled an assessment of the impact and suitability of a specific type of varnish for flexographic printing.

2. EXPERIMENTAL SETTINGS AND METHODS

2.1. Swelling of the photopolymer material

Swelling is common phenomena in the printing process. The deformation of the photopolymer printing plate is caused when the ink and solvents enter the material, resulting with problems in the printing process. In Figure 1, an infographic of the result of swollen photopolymer printing plate can be seen.



Figure 1: Infographics of swollen photopolymer; a) swollen photopolymer that leads to deformation of printing elements, b) normal, un-swollen photopolymer with stable printing elements

Problems that occurs due to the swelling are:

- a) Lack of register (misalignments of printing elements, poor pre-press calibration and colour imperfection)
- b) Problems with tolerances in the printing machine
- c) Poor print quality (distortion, errors, overlaps that can occur on the final product)
- d) Costs (decreased sleeve lifespan that causes more frequent sleeve replacing, additional cost of maintenance, poor print quality that leads to repetition of entire process, loss of customer)
- e) Dot gain due to swollen or deformed plates. It occurs most likely with use of aggressive inks, solvents, cleaners that cause the plates to swell (Jenkins, 1985; Liu et al, 2013).

In this experiment, swelling of the photopolymer sample was carried out in four varnishes mentioned in 2.1. Swelling experiments were performed until the equilibrium (normalized degree of swelling) was reached (Tomašegović et al, 2016). Measurements were performed by gravimetric method using analytical scale Mettler Toledo XS205 (MT laboratories, n.d.) in a controlled environment with a constant temperature of 23°C and relative humidity of 55±2 %.

Photopolymer samples were immersed in varnishes for periods up to 300 minutes, after which the weighing showed that the equilibrium of swelling was reached. Normalized swell ratio (Mt) for control periods of 5, 20, 40, 80, 120, 180, 240 and 300 minutes of immersion was calculated using Equation 1:

$$M_t = \frac{m_t - m_0}{m_0} \cdot 100\% \tag{1}$$

where m_t stands for the weight of the swollen polymer at a time t, and m_0 for the weight of the dry polymer sample before the immersion. Before each weighing, samples were quickly cleaned with acetone which causes minimal photopolymer swelling (Tomašegović, 2016). Swelling dynamics of the photopolymer material due to the effects of the varnishes was observed.

2.2. Contact angles of varnishes and surface free energy of photopolymer

Contact angle (Figure 2) is a quantitative measure of wetting of solid surface with a liquid. It can be described geometrically as the angle formed by the tangents on liquid drop and the solid surface at the three-phase boundary where a liquid, gas and solid come in contact. One can divide contact angles to static and dynamic one. The difference between contact angle hysteresis is referred as advancing or receding contact angle.



Figure 2: Difference between two contact angles of inks on flexographic printing element: a) low contact angle, b) high contact angle

This feature is important and connected to surface wettability. High wettability results from the higher surface energy of solid that pulls the liquid down with strong attracting force. This feature makes the droplet to spread out on the solid surface. The surface tension of the liquid in this case is weaker than the surface free energy of the solid. Wetting is important for high-quality and stable printing process (Tryznowski et al, 2018).

For this research, static contact angles of four varnishes were measured on the surface of a classic, styreneisoprene-styrene based LAMS printing plate. Used varnishes were matt and gloss water-based (waterdispersive) varnish, oil-based and UV varnish. Contact angles were measured using Dataphysics OCA30 goniometer and its program support. Static contact angle of varnishes on the printing plate were measured using the needle-in sessile drop method, with the volume of the drop of 10 μ l. Measurements were taken at the point of the stabilization of the drop on the polymer surface.

Surface free energy of the printing plate was calculated using the contact angles of three probe liquids (water, diiodomethane and glycerol) and OWRK method (Owens et al, 1969). Volume of the probe liquid drops was 1 μ l, and the sessile drop method was used. Measurements of the contact angle were taken 4 seconds after the initial contact of the liquid and solid.

2.3. FTIR-ATR spectroscopy and microscopy

In order to analyse the chemical changes in the surface layer of the printing plate samples after swelling, FTIR-ATR spectra of the photopolymer in transmittance mode was collected. Since the FTIR-ATR method provides the information about the vibrations of certain chemical bonds only in the depth of 1-2 μ m of the analysed sample, changes in the spectra could be used to explain the changes occurring in the surface layer of the material after the exposure to different varnishes (Tomašegović, 2016).

In order to check for the possible visible damage and changes on the photopolymer surface caused by the immersion in varnishes, microscopy of the printing plate surface was performed before and after the immersion in varnishes. Olympus BX51 microscope was used for this purpose, and the magnification was set to 200x (Olympus, n.d.).

3. RESULTS AND DISCUSSION

3.1. Swelling of the photopolymer material

Swelling experiments were performed in order to assess the resistance of the photopolymer to the specific varnish, i.e. to determine if the varnish penetrates the photopolymer matrix and/or partially dissolves it. Figure 3 presents the dynamics of photopolymer swelling in different varnishes. Water-based varnishes have a negligible impact on the tested material – maximal normalized degree of swelling is cca. 0.5% of the solid sample weight (Figure 3a) – b). After 300 minutes of the immersion, swelling equilibrium is reached. In Figure 3c, one can see the dynamics of swelling of the sample immersed in the UV-curable varnish. It is visible that the swelling process starts to slow down after cca. 200 minutes, and that the normalized degree of swelling reaches 1.1% after 300 minutes. This is acceptable from the point of the graphic reproduction process, but it is evident that the swelling process continues even after 5 hours. Therefore, the interaction of the UV varnish and flexographic printing plate should be monitored for higher run lengths.



Figure 3: Swelling dynamics of the photopolymer immersed in different varnishes: a) water-based matt varnish, b) water-based gloss varnish, c) UV-curable varnish, d) oil-based varnish

Oil-based varnish causes significant swelling of the photopolymer material (Figure 3d). The swelling process starts to slow down after 250 minutes, but normalized degree of swelling reaches 15.2% after 300 minutes without achieving equilibrium. One can conclude that the solubility parameters of this oil-based varnish and the photopolymer used in this research are too similar (Hansen, 2007) for the varnish to be used in the reproduction system that includes tested printing plate.

3.2. Contact angles of varnishes and surface free energy of photopolymer

In order to address the effect of the prolonged exposure of the photopolymer to the varnishes, wettability of the varnishes on the photopolymer surface was assessed by the contact angle measurements. Furthermore, surface free energy (SFE) of the photopolymer not exposed to the varnishes was compared to the surface free energy of exposed ones.

Figure 4. presents the contact angles of the varnishes on the photopolymer surface. It is visible that the water-based gloss varnish displays the best wettability of the photopolymer among tested varnishes, and the oil-based varnish the poorest one. Poor wettability of the oil-based varnish on the photopolymer could be assigned to the air-polymerization of the oil-based coating, and to its thickness.

Since the water-based flexographic varnishes are basically dispersions of the acrylic resin in water and some alcohol, their primary drying mechanism is by coalescence (Resino, n.d.). Therefore, due to the separation of the water and resin part, wetting of these varnishes on the flexographic printing plate is not poorer than that of the UV-varnish.



Figure 4: Contact angles of varnishes on the printing plate

In Figure 5. one can see the total SFE of the photopolymer samples exposed to the swelling in varnishes, compared to the non-swollen sample.

It is visible that the immersion of the photopolymer in the varnishes for 5 hours does not affect the total SFE drastically, except for the oil-based varnish. Since weighing showed the photopolymer remains swollen even 24 hours after the immersion in the oil-based varnish, the drastic increase of the surface free energy can be assigned to the presence of the varnish molecules inside the photopolymer matrix.

Since the photopolymer material used in this research is a low-polarity type of material, all the changes of the total SFE are closely followed by the changes of the dispersive SFE.

The decrease of the total (and dispersive) SFE after the immersion in water-based and UV varnishes points to two possibilities: the degradation of the photopolymer and/or migration of the low-molecular weight waxes from the volume of the material to its surface (Matsubara et al, 2011).



Figure 5: Total surface free energy of the printing plate after the immersion in varnishes

Polar SFE of the photopolymer before the swelling is close to 0 (0.01 mN/m). After the immersion in the varnishes and drying (Figure 5c), polar SFE slightly increased for all samples. However, this increase still results with very low values (< 0.8 mN/m). It can be concluded that, based on the types of changes of photopolymer's SFE, all tested varnishes except for the oil-based one should be suitable for application in the graphic reproduction with used printing plate.

3.3. FTIR-ATR spectroscopy and microscopy of the photopolymer surface

Figure 6. presents the FTIR-ATR spectra of the photopolymer samples taken after they were immersed in the varnishes for 5 hours and left to dry for 24 hours. The wavelength ranges presenting the changes in the vibrations of the types of chemical bonds are shown in Figures 6a) and 6b).



Figure 6: FTIR-ATR spectra of the photopolymer after swelling in varnishes: a) wavelength range of 1300 - 1500 cm⁻¹, b) wavelength range of 2800 - 3000 cm⁻¹

Figure 6a) presents the first wavelength range of interest: $1300 - 1500 \text{ cm}^{-1}$. It is visible that the samples which have been immersed in water-based varnishes present two peaks which are not prominent for the other samples: one at 1462 cm⁻¹ and the other at 1472 cm⁻¹. They correspond to the aromatic C=C stretch. Other distinctive peak at 1378 cm⁻¹ for the sample immersed in water-based gloss varnish corresponds to the CH₃ and CH₂ bending, or the C-H methyl rocking in the alkenes (Bardakçı, 2007). Since these peaks are not present for all photopolymer samples, it can be concluded that their presence presents the changes caused by residual of the varnishes in the photopolymer surface layer.

The peak at 1404 cm⁻¹ is more pronounced for the sample immersed in UV varnish, and corresponds to the symmetrical C=O stretch (Kumar Trivedi et al, 2015). Since this peak is present in all analysed spectra, it can be concluded that it presents the changes occurring in the material structure as a direct consequence of the exposure to the varnishes. Likewise, all peaks in Figure 6b) are present for all samples, but display different transmittance. These peaks are characteristic for the tested photopolymer material. Peak at 3005 cm⁻¹ corresponds to the =C-H stretch and points to the increased unsaturation in the sample after treating it with water-based gloss varnish. Peaks at 2849 cm⁻¹ and 2916 cm⁻¹ correspond to the C-H stretching in alkanes. Their decreased transmittance after treating the material with water-based varnishes could point to the migration of the waxes from the bulk of the photopolymer to the surface – and therefore the decreased SFE. This explanation could be applied for the peak at 2875 cm⁻¹, as well – it is present only for the samples treated with water-based varnishes and corresponds to the C-H stretching vibration.

The increased transmittance of these peaks after treating the photopolymer with UV and oil-based varnishes indicates that these varnishes do not cause the migration inside the material. However, they do affect the surface structure by decreasing the amount of the present characteristic C-H bonds, possibly by dissolving the compounds from the surface layer and/or incorporating in the material structure (Tomašegović, 2016).

Microscopic images of the photopolymer surfaces were taken after the swelling in the varnishes and drying. Images presented in Figure 7. were taken in the transmission light, with the magnification of 200x.

Figure 7a) presents the photopolymer surface that has not been immersed in the varnish. One can see the initial surface texture on the sample. Figure 7b) presents the photopolymer surface after it has been immersed in water-based matt varnish. The appearance of the surface is slightly changed which corresponds to the decrease of the dispersive (and total) SFE (Figure 5), but no signs of the significant material dissolving/damage are evident.



Figure 7: Surface of the photopolymer after swelling in varnishes at 200x magnification: a) non-immersed sample, b) immersed in water-based matt varnish, c) immersed in water-based gloss varnish, d) immersed in UV-curable varnish, e) immersed in oil-based varnish

In Figure 7c), which presents the photopolymer surface after the immersion in water-based gloss varnish, one can notice the subtle signs of the surface damage in form of the cracks on the material. Since the water-based gloss varnish causes the most prominent decrease of the total and dispersive SFE of the photopolymer among the used varnishes, it could be concluded that the visible material degradation takes place on the surface. These changes are corresponding to the changes in FTIR-ATR spectra presented in Figure 6.

UV varnish, on the other hand, causes the visible *pitting dissolution* on the photopolymer surface (Figure 7d). Based on the results of the swelling experiments, the changes of the surface free energy and FTIR-ATR spectra, it can be concluded that UV flexographic varnish penetrates the photopolymer material, and causes both swelling and partial dissolution.

Finally, the effect of the oil-based varnish on the photopolymer can be observed in Figure 7e). No prominent degradation is evident after the immersion. However, oil-based varnish caused the extensive swelling of the material and stayed incorporated in the photopolymer even after 24 hours.

4. CONCLUSION

The aim of this research was to characterize the influence of common varnishes used in graphic reproduction on the photopolymer material flexographic printing plate is made of. After immersion in the varnishes for defined period, changes in the plate's surface free energy components was observed, as well as the visible changes on the material surface.

It can be concluded that water-based and UV-curable varnishes can be used in the reproduction system with expected changes of the printing plate's SFE under 6%. Water-based varnishes cause noticeable decrease of the photopolymer's SFE. The decrease of the total (and dispersive) SFE after the immersion in water-based and UV varnishes points to two possibilities: the degradation of the photopolymer and/or migration of the low-molecular weight waxes from the volume of the material to its surface.

Swelling of the photopolymer in water-based varnishes was negligible, while the normalized degree of swelling reached 1.1% for UV-curable varnish.

Oil-based varnish affected the photopolymer material by causing prominent normalized degree of swelling that reached 15% after 5 hours. Furthermore, oil-based varnish remained in the photopolymer structure and caused the increase of total and dispersive SFE by cca. 30%. FTIR-ATR spectra showed that all varnishes affect the chemical bonds in the photopolymer surface, either by remaining integrated in the material, or by directly causing the changes in the material structure.

Based on the results obtained in this research, it can be concluded that the effects of the varnishes used to print with flexographic printing technique should definitely be monitored depending on the run length, in order to avoid the possible problems with coating quality as a result of the printing plate's surface changes and degradation.

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