Customization of flexographic printing plates related to uvc-induced changes in the crosslinking degree

Tamara Tomašegović[1*], Sanja Mahović Poljaček[1], Mirela Leskovac[2]

[1] University of Zagreb Faculty of Graphic Arts, Croatia

[2] University of Zagreb Faculty of Chemical Engineering and Technology, Croatia

[*] E-mail: ttomaseg@grf.hr

Abstract

In this paper, the swelling properties of photopolymer flexographic printing plates related to the variations of UVC post-treatment have been analysed. The aim of the research was to interconnect the changes in the crosslinking degree of the photopolymer material occurring due to the modified UVC radiation of the printing plate and the changes of its surface free energy crucial in the graphic reproduction process. Changes in the crosslinking degree in the photopolymer materials have been analysed by the swelling experiments. Results have proven that the partial dissolution of the photopolymer material caused by the immersion of the printing plates in various solvents is in the direct relation with the changes of the dispersive surface free energy. UVC post-treatment, used for the crosslinking termination and the definition of the surface properties of printing plates, is therefore directly affecting the resistivity of the printing plate in the solvent environment. By calculating the correlation coefficients for the weight loss of the photopolymer material in solvents and the dispersive surface free energy, the relation between the crosslinking degree and the UVC post-treatment has been established.

Keywords: photopolymer, flexography, UVC post-treatment, swelling, crosslinking, surface free energy.

1. Background

Flexography is a printing technique used primarily in the packaging production and novel applications in functional printing. It utilizes a photopolymer printing plate that deforms elastically during the engagement in the printing process, therefore enabling the optimal contact with the printing substrate and transferring of the image (*Kipphan, 2001, Page Crouch, 1998*).

Modern flexographic printing plates can be solvent-washable or water-washable and are based on the effect of crosslinking as a result of the exposure to UVA wavelengths that initiate crosslinking and UVC wavelengths that terminate it, thus giving large and stable molecular structures insoluble in the defined rinsing solution. Composition of this type of printing plates includes different types of copolymers, most common styrene-butadiene-styrene (SBS) and styrene-isoprene-styrene (SIS) block copolymers, photoinitiators sensitive to UV radiation, colorants and other additives (*Knoll, 2002*). Specifically, some photopolymer printing plates have low-molecular weight carbohydrate compounds added to their composition.

The role of these compounds is to migrate to the surface of the photopolymer and protect the material from the destructive influence of the oxygen and ozone during the printing plate production.

Laser Ablation Mask Layer (LAMS) technology is the most common and widely adopted principle used in the printing houses for production of flexographic printing plates. The process of flexographic printing plate production based on LAMS is presented in Fig. 1.

The base of the photopolymer flexographic printing plates is made of polyethylene terephthalate (PET), on which the photopolymer material has been applied (Fig. 1.a). LAMS mask covers the whole surface of the printing plate. It enables the transfer of the image to the printing plate by the ablation process. After the back exposure is performed in order to create the base layer for the printing elements (Fig.1.b), LAMS is removed by laser ablation from the image parts of the photopolymer material (Fig. 1.c). Fig. 1.d) presents the main exposure to UVA radiation, where printing and

nonprinting areas are formed. Exposed parts crosslink and become insoluble in the defined rinsing solution (organic solvent or water).
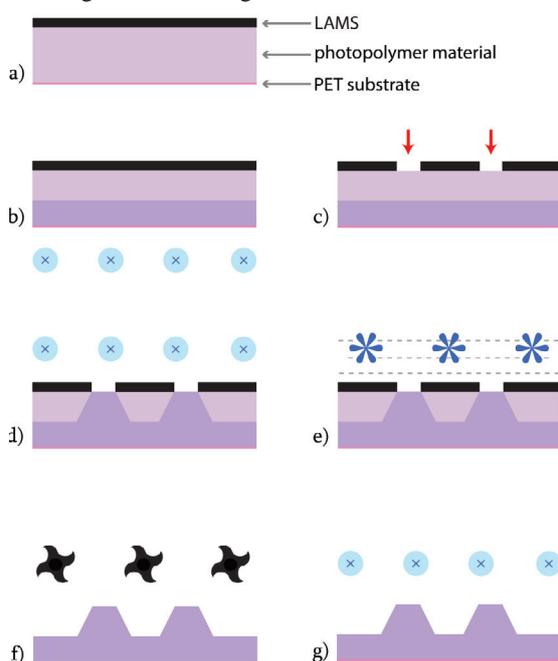

Figure 1. Production of the LAMS-based flexographic printing plate: a) photopolymer sheet prepared for the image transfer, b) back exposure, c) ablation of the LAMS, d) main exposure, e) rinsing, f) drying, g) post-treatment

After the main exposure, follow the rinsing of the unexposed parts in the photopolymer material (Fig. 1.e) and drying (Fig. 1.f). Printing plate is finished after the post-treatment when it is exposed to UVA and UVC radiation (Fig. 1.g) in order to terminate the crosslinking process and obtain the optimal surface properties (*Tomašegović, Mahović Poljaček and Cigula, 2013, Lee et al., 2004*).

Specifically, UVC post-treatment, as the last step in the printing plate production process, defines the final surface properties of the printing plate. Surface free energy (γ) of the printing plate needs to be adjusted to the surface tension of the used printing ink in order to obtain the optimal quality of the print. UVC post-treatment can be used as a tool for the modification of the printing plate's surface properties in order for it to meet the specific requirements (*Tomašegović et al., 2016*), but it needs to be carefully adjusted since it causes the changes in the photopolymer surface structure. Previous research has shown that, depending on the type of the photopolymer material, UVC

radiation causes some further crosslinking in the printing plate before the termination process (*Tomašegović, Mahović Poljaček and Leskovac, 2016*). In this research, the influence of the UVC post-treatment on the changes in the crosslinking degree in the photopolymer surface layer and consequently the changed surface properties were analysed by means of the swelling experiments. The changes in the swelling behavior differed according to the type of the photopolymer material. The results of the swelling experiments were interconnected with the changes in the material's surface structure and properties, enabling the analysis of the resistivity of the photopolymer to different solvents and the definition of the influence of UVC post-treatment on γ of the flexographic printing plate.

2. Experimental

2.1. Preparation of samples

For this research, three different photopolymer materials were tested in terms of their swelling and surface properties which are subject to change due to the variations in the post-treatment process. All types of printing plates were LAMS-based, with digital (CtP) production procedure. Two types of printing plates were commonly used solvent-washable, and one type was water-washable printing plate (Fig. 2). In this paper the ACE Digital, Digital MAX, and Cosmolight QS samples were used. All samples of printing plates were produced by the standard procedure recommended by their manufacturer (*MacDermid Digital MAX photopolymer plate, Flint ACE Digital photopolymer plate, Toyobo Cosmolight photopolymer plate, 2016*), up to the post-treatment process.
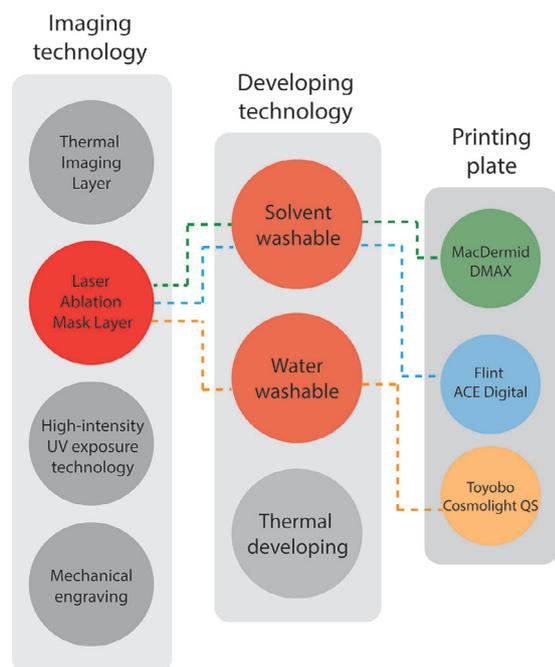
Figure 2. Types of flexographic printing plates

After the stabilization period, produced printing plate samples were exposed to the UV post-treatments. The purpose of this research was to maintain the necessary functional properties of the flexographic printing plates. Therefore, both UVA and UVC post-treatments were performed on the samples (except the first, referent sample without any post-treatment), but the duration of the UVC post-treatment was varied. The duration of the UVA post-treatment was kept constant at optimal duration recommended by the manufacturers (10 minutes) (*MacDermid Digital MAX photopolymer plate, Flint ACE Digital photopolymer plate, Toyobo Cosmolight photopolymer plate, 2016*). The duration of the UVC post-treatment was varied from 0 to 20 minutes, with the step of 1 minute.

2.2. Methods and devices

Method of material swelling has been used for the analysis of the photopolymer material's crosslinking properties. This method is applicable for the characterization of changes in the portion of non-crosslinked compound in the material and as a control method for testing the resistance of the material to solvents. Specifically, the fully crosslinked structures display decreased degree of swelling compared to non-crosslinked structures, and no partial

dissolution in solvents (*Krongauz and Trifunac, 2013*).

Swelling measurements were performed by gravimetric method (*Liu et al., 2013*), in a controlled environment with a constant temperature of 25°C. Ethyl acetate (ACS grade), toluene (ACS grade) and acetone (ACS grade) were used as a swelling agents due to the different types and strengths of their molecular bonds, and therefore different impact on the photopolymer material. Named swelling agents cause swelling and partial dissolving of the photopolymer material used in the printing plate production. Furthermore, ethyl acetate has a regular application in flexography, specifically in the composition of printing inks and as a solution for cleaning the ink from the printing plate (*Kaoru et al., 1975*). Its usage needs to be therefore regulated in terms of the concentration in the ink and washing agents. Swelling properties of the photopolymer material in acetone and toluene were used to obtain a detailed insight into the photopolymer swelling behavior.

Photopolymer samples were immersed in the ethyl acetate, toluene and acetone for periods up to 420 minutes, after which the weighing showed that the equilibrium of swelling was reached. Degrees of swelling (*Mt*) for control periods of 5, 15, 30, 60, 90, 120, 180, 300 and 420 minutes of immersion were calculated using Eq. 1:

$$M_t = \frac{m_t - m_0}{m_0} \cdot 100\% \qquad (1)$$

where *mt* presents the weight of the swollen polymer at a time *t*, and *m0* the weight of the dry polymer sample before the immersion. After immersions, samples were dried at 80 °C by means of OHAUS MB 45 moisture analyser. The solvent ratio in the sample decreased to 0.23% and stabilized. Samples were then weighted again to determine the weight loss after the swelling.

On the printing plate samples contact angles of different probe liquids and surface free energy were calculated by means of goniometer Data Physics OCA 30 (*Dataphysics OCA 30, 2016)*. Contact angle and surface free energy of the probe liquids are the parameters which are then used to calculate the surface energy of the printing plate samples. Three probe liquids of

known surface energy were used for the measurements: water, glycerol and diiodomethane (Table 1.). Contact angle was measured using Sessile drop method, ten times on each sample, on the different parts of the printing plate.

Table 1. Surface free energy (γ_{lv}) and their dispersive (γ^d_{lv}) and polar (γ^p_{lv}) components for probe liquids

Liquid	Surface free energy (mNm¹)		
	γ_{lv}	γ^d_{lv}	γ^p_{lv}
Diiodomethane (Ström et al.)	50.8	50.8	0.0
Glycerol (van Oss et al.)	64.0	34.0	30.0
Water (Ström et al.)	72.8	21.8	51.0

The shape of the probe liquid drops was a spherical cap, and the volume of the drops was 1 μm³. All measurements of the contact angle on the samples were performed in the same moment after the drop touched the photopolymer surface - with delay of 10 frames, and the average values were calculated (*Owens and Wendt, 1969*).

Surface free energy was calculated using OWRK method, applicable for polymer, aluminum and coatings characterization (*Owens and Wendt, 1969*). After obtaining the values of contact angles for each probe liquid, mean values of contact angle for each sample were calculated. Results of the contact angle measurements enable calculation of the surface free energy, its polar and dispersive component (Eq. 2):

$$\frac{(1-\cos\theta)\cdot\gamma_s}{2\sqrt[2]{\gamma_l^d}} = \sqrt{\gamma_s^p}\sqrt{\frac{\gamma_l^p}{\gamma_l^d}} + \sqrt{\gamma_s^d}$$

(2)

where γ*s* is surface tension of the solid, γ_l is the surface tension of the liquid, γ^d disperisve part of surface tension, γ^p polar phase of surface tension, and θ is the contact angle (*Van Oss et al., 1993*).

3. Results

3.1. Swelling properties of flexographic printing plates

Swelling experiments on photopolymer samples were performed in order to get an insight into the changes of photopolymer's cohesion parameters as a result of the UVC post-treatments. When immersing the sample in the solvents of known solubility parameters, normalized degrees of swelling (Eq. 1) provide the

information about the "compatibility" of the material and the specific solvent. Similar cohesion parameters of the immersed material and solubility parameters of solvent result in higher swelling degree and possible partial dissolving (*Miller-Chou and Koening, 2003*). Results of swelling experiments are presented in Fig. 3.- 5.

Normalized swelling degrees for UVC post-treated ACE Digital samples can be observed in Fig. 3. One can see that prolonged UVC post-treatment causes increase of swelling degree in acetone (Fig. 3.a), which points to the increased compatibility of forces in the material and the forces in the acetone, and is an indicator of the changes in strength of chemical bonds in photopolymer material. The highest value of swelling degree in acetone is 13.94%, and is visible for the sample treated for 20 minutes of UVC post-treatment.

Swelling degree in ethyl acetate (Fig. 3.b) decreases with prolonged UVC post-treatment compared to the not treated sample, which is a valuable information if using inks and plate washing agents with ethyl acetate in their composition. Maximal normalized swelling degree in ethyl acetate depending on the duration of UVC post-treatment is 9.93% for not treated sample.

Swelling behavior in toluene (Fig. 3.c) shows the most expressed swelling degree. Until 10 minutes of UVC post-treatment, swelling degree decreases, and then starts to increase, reaching 155.01% for 20 minutes of UVC post-treatment.
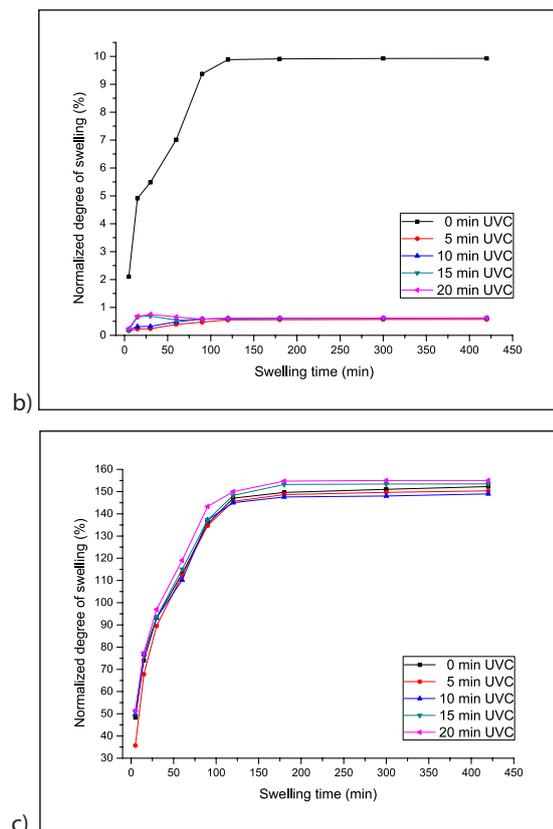

a)

b)

c)
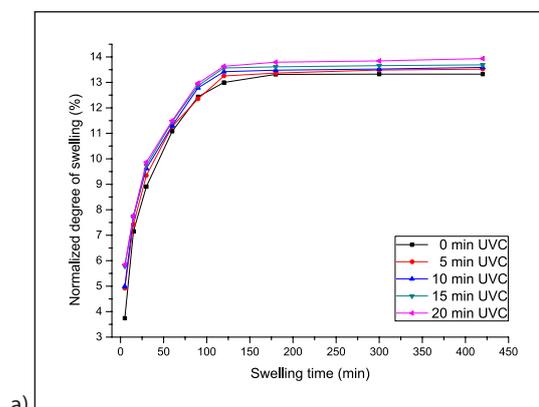
Figure 3. Normalized degrees of swelling for UVC post-treated ACE Digital samples immersed in: a) acetone, b) ethyl acetate, c) toluene

Fig. 4. presents the normalized degrees of Digital MAX photopolymer swelling in different solvents depending on durations of UVC post-treatment. It is worth noticing that the general behavior of photopolymer swelling shows the similar trend for immersion in all solvents, but with different normalized swelling degree. Generally, the degree of swelling decreases with UVC post-treatment of durations up to 10 minutes and then increases, reaching the equilibrium. Normalized degree of swelling in acetone (Fig. 4.a) reaches a maximum of 15.23% for 20 minutes of UVC post-treatment. On the other hand, swelling in ethyl acetate (Fig. 4.b) is less expressed, with maximum of 1.19% for sample treated with UVC post-treatment for 20 minutes.

General increase of the normalized degree of swelling after 10 minutes of UVC post-treatments can be associated with the changes in the surface free energy caused by UV radiation, since the solvent first needs to penetrate the surface of the photopolymer material. However, the maximal normalized degree of swelling

in toluene is, similar to other tested photopolymer materials, 10.78 times higher than in acetone and 142.48 times higher than in ethyl acetate (Fig. 4.c).
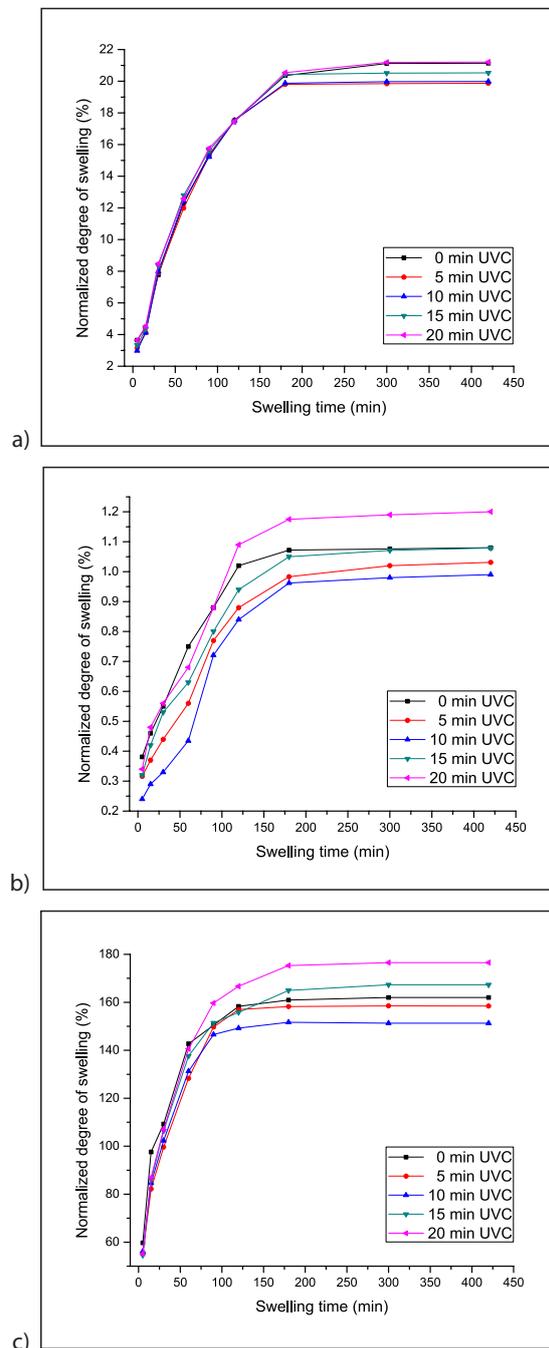

a)

b)

c)

Figure 4. Normalized degrees of swelling for UVC post-treated Digital MAX samples immersed in: a) acetone, b) ethyl acetate, c) toluene

Fig. 5. displays the results of swelling experiments for Cosmolight QS samples. UVC post-treatment displays the similar influence on swelling behavior in different solvents, with maximal values obtained for samples treated with longest durations of post-treatments.

Maximal swelling degrees in acetone is 13.80% for sample treated for 20 minutes of UVC post-treatment (Fig. 5.a). Ethyl acetate causes the maximal swelling degree of 2.02% for 20 minutes of UVC post-treatment (Fig. 5.b). Swelling degree in toluene displays the highest value of 149.87% after 20 minutes of UVC post-treatment (Fig. 5.c). A trend that is not generally increasing is present in the swelling degrees of samples immersed in ethyl acetate, with the exceptions of the untreated sample.

For all other samples immersed in ethyl acetate, there is an initial decrease of the swelling degree up to 30 minutes of the immersion period.
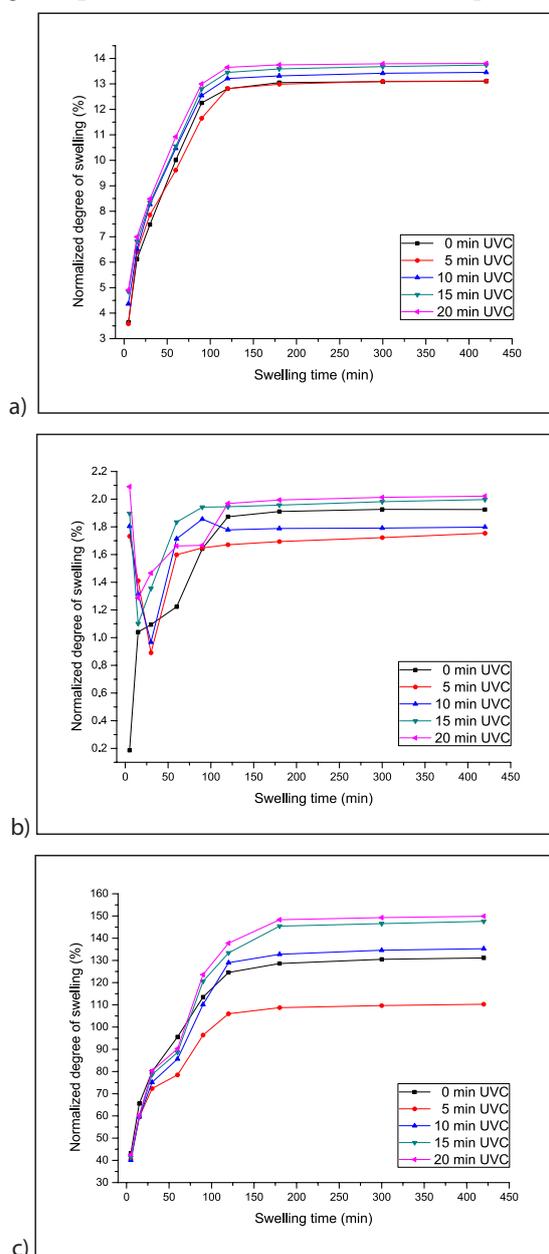

a)

b)

c)

Figure 5. Normalized degrees of swelling for UVC post-treated Cosmolight QS samples immersed in: a)

acetone, b) ethyl acetate, c) toluene

This dynamic of ethyl acetate's penetration in Cosmolight QS samples indicates that in the first 30 minutes, solvent slowly penetrates the surface layer of the material, which is affected by UVC post-treatment. Changed surface properties of the photopolymer material after the UVC post-treatment manifest in modified cohesion parameters in the photopolymer surface layer, compared to the core of the material (*Sefton and Merill, 2003*).

3.2. Weight loss of flexographic printing plates after immersion in solvents

Results of swelling properties of photopolymer materials enabled the comparison of the relative differences in the cohesion forces in photopolymer materials that were immersed in solvents of different solubility parameters (Fig. 3. – 5.). Dynamics of swelling with prolonged UVC post-treatments pointed to the possible expressed differences between the surface and the core of the photopolymer material.

The results of swelling experiments were used to calculate the weight loss of the samples after immersion in different solvents and drying. Segments in the core of photopolymer materials' composition which are soluble in used solvents would cause the weight loss after the immersion and drying. Increased crosslinking degree in the material should result with the decreased weight loss (*Crompton, 2006*). However, since the UV post-treatments affect differently the surface and the core of the material, changes in weight loss differ for the samples treated with varied durations of UVC post-treatments. In this way, degradation by erosion of the surface, expressed during the swelling experiments could be detected and analysed.

Fig. 6.a. presents the weight loss of ACE Digital samples immersed in different solvents. One can see that UV post-treated samples of ACE Digital material show the increasing trend of weight loss in toluene. This points to the expressed compatibility of cohesion forces in the material and solubility parameters of toluene.

Immersion of ACE Digital photopolymer material in acetone and ethyl acetate causes the similar weight loss behavior (Fig. 6.a). It can be concluded that the unsaturation in not UV

post-treated sample or compounds that haven't participated in the crosslinking reactions cause the partial dissolution. Weight loss then decreases up to 15 minutes of the UVC post-treatment, but then increases again. This indicates that prolonged UVC post-treatment results with breakage of bonds in photopolymer structure and/or formation of residuals soluble in acetone and ethyl acetate.
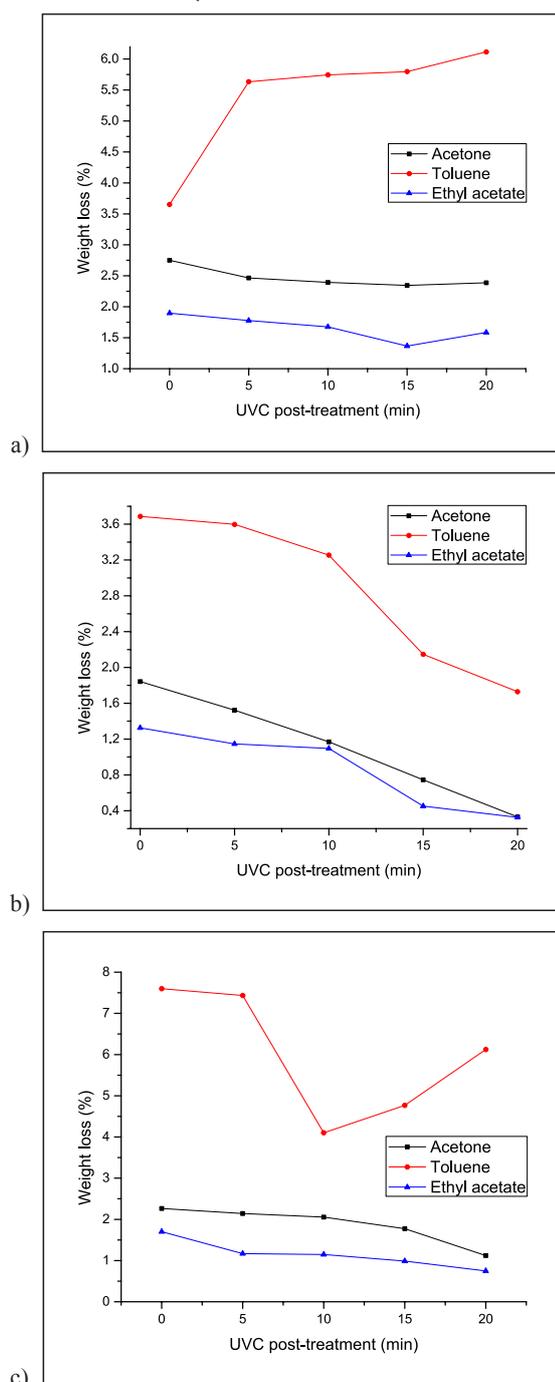

a)

b)

c)

Figure 6. Weight loss of photopolymer materials immersed in different solvents after varied UVC post-treatment: a) ACE Digital, b) Digital MAX, c)

Cosmolight QS

Fig. 6.b displays the weight loss of Digital MAX photopolymer materials after immersion in different solvents. Expressed decrease of weight loss in toluene at prolonged UVC post-treatment points to the conclusion of both increased crosslinking degree and the positive changes in cohesion parameters in the material. The material shows the decreased weight loss in all used solvents after prolonged UVC post-treatment. Weight loss in acetone and ethyl acetate decreases to approx. 0.3% after 20 minutes of UVC post-treatment.

Weight loss of Cosmolight QS photopolymer material (Fig. 6.c) displays the decreasing trend for the samples immersed in acetone and ethyl acetate, pointing to the increased crosslinking degree in the material after prolonged UVC post-treatments. However, since toluene showed the highest compatibility with tested photopolymer materials in terms of the swelling degree, the increased weight loss after 10 minutes of UVC post-treatment is indicative.

It is known that the UV radiation of the photopolymer causes different changes in the surface layer of the material and the core of the material (*Cheremisinoff, 1996*). Therefore, the trends of the changes in weight loss of photopolymer materials immersed in different solvents require the analysis in connection with the changes in γ of photopolymer material, specifically in relation to changes of γ^d which is in the direct relation with the crosslinking degree (*Miller-Chou and Koening, 2003, Sefton and Merill, 2003*).

3.3. Surface free energy of flexographic printing plates

Calculations of the surface free energy (γ^{total}) and it dispersive (γ^d) and polar (γ^p) components showed that the variations of the UVC post-treatment have different effects on the tested photopolymer material samples (Fig. 7.).

When performing the variation of UVC radiation from 0 to 20 minutes, γ^{total} (Fig. 7.a) of the photopolymer surface for ACE Digital samples reaches maximal value of 34.81 mNm^{-1} at 5 minutes of UVC post-treatment and then decreases to 26.16 mNm^{-1} for 20 minutes of UVC post-treatment. Cosmolight QS samples display similar behavior, reaching maximal value

of γ^{total} of 32.39 mNm^{-1} at 10 minutes of UVC post-treatment and then decreasing to 30.18 mNm^{-1} for 20 minutes of UVC post-treatment. Digital MAX samples display the constant increase of γ^{total} from 33.5 mNm^{-1} to 41.2 mNm^{-1}.

The trends of changes of γ^{total} after prolonged UVC radiation are primarily caused by the changes of γ^{d} (Fig. 7.b). The increase of γ^{d} and γ^{total} of photopolymer material can be explained by further crosslinking which occurs in the photopolymer material and indicates that, even after the printing plate is considered to be finished in its production process, further crosslinking caused by UVC radiation before the termination takes place. The inflexion point at 5 minutes of UVC post-treatment for γ^{total} and γ^{d} for ACE Digital sample and after 10 minutes for Cosmolight QS samples can be explained both by the migration of the low-molecular weight carbohydrates to the surface and by weaker intermolecular forces in the polymer network due to the start of the material degradation (*Krásný, Kupská, and Lapčík, 2012*).
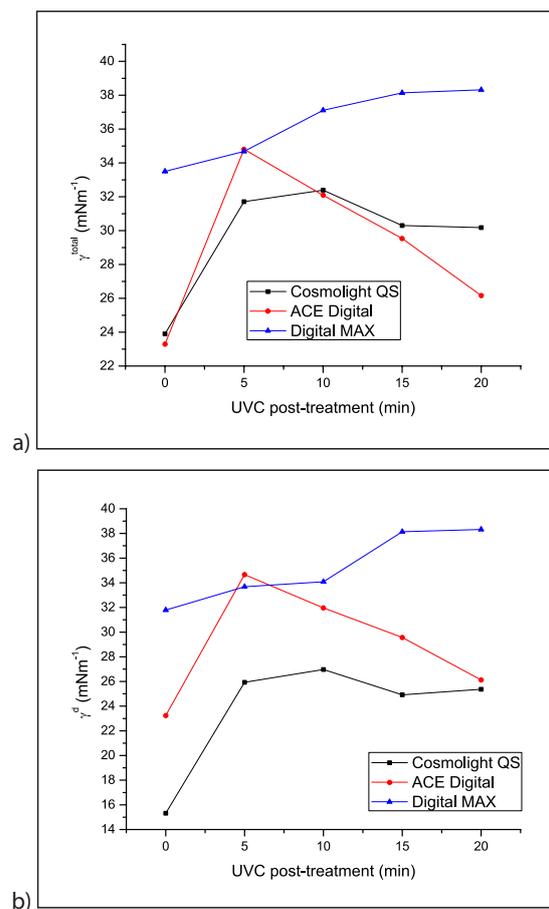
c)

Figure 7. Surface free energy of printing plate samples exposed to varied UVC post-treatment: a) total surface free energy (γ^{total}), b) polar surface free energy (γ^{p}), c) dispersive surface free energy (γ^{d})

Changes of γ^{p} are not as expressed as changes of γ^{d} (Fig. 7.b - c). As photopolymer materials used as flexographic printing plates have the low initial values of γ^{p}, its influence on γ^{total} is not as significant. However, even though γ^{d} is a dominant component influencing γ^{total}, changes in γ^{p} have an interesting trend. γ^{p} for all samples displays an inflexion point after initial increase after which it decreases to a certain level, depending on the photopolymer material. Initial increase of γ^{p} is caused by the integration of the oxygen in the surface layer of photopolymer material (*Deflorian, Fedrizzi and Rossi, 1998, Controlled Radical Polymerization Guide, 2016*). However, the decrease of γ^{p} after the certain duration of UVC post-treatment can be explained by the process of migration of non-polar carbohydrate compounds of low molecular weight (such as protective waxes added to some types of photopolymers) to the surface of the material. This migration process influences the swelling behavior and the weight loss of photopolymer material (*Knoll, 2002*).

Finally, the changes of printing plate's γ and its components due to the UVC radiation are significant for the graphic reproduction process because of the changes in the adsorption of the printing ink on the printing plate.

4. Discussion

The specific swelling and weight loss behavior of each type of photopolymer material tested in this research can be related to the changes in the surface free energy.

a)

b)

Obtained results of the swelling experiments are dependent on the solubility parameters of used solvents (*Hansen, 2007*), presented in Table 2. They are specific for each solvent and predict if the observed material will form a solution with another material. The closer the solubility parameters of observed material and solvent, the more that material is likely to swell and partially dissolve in that solvent.

Obtained results indicated that there is the highest compatibility of the forces inside the tested photopolymer materials and toluene due to the expressed swelling degree (Fig.3. - 5.).

Observing Table 2., one can conclude that this compatibility manifests due to the highest dispersion forces in toluene, and weak hydrogen bonding capability, which is in consonance with the flexographic photopolymers' basic composition. The swelling behaviors of photopolymer printing plates in acetone and ethyl acetate point to the conclusion that they do not display the hydrogen bonding capability (*Loadman, 2012*).

Table 2. Hansen solubility parameters for solvents used in swelling experiments

Hansen parameters for solvents at 25 °C (MPa$^{1/2}$)	Acetone	Ethyl acetate	Toluene
Total Hildebrand parameter (∂_t)	20	18.1	18.2
Dispersion component (∂_d)	15.5	15.8	18
Polar component (∂_p)	10.4	5.3	1.4
Hydrogen bonding component (∂_h)	7.0	7.2	2.0

Swelling behavior together with weight loss of photopolymer materials needs to be observed in terms of the two-phase system with expressed differences in their physicochemical properties: surface and the core of material. The surface layer of the material undergoes the photo oxidation process when exposed to UVC radiation, while the core undergoes the further UV-induced crosslinking (*Sefton and Merill, 2003*).

Since swelling experiments showed that solubility parameters of acetone are not particularly compatible with tested photopolymer materials (Fig. 6.), the weight loss in acetone is not affected by the changes in the composition and the structure of the surface layer. The decreasing trend of the weight loss in acetone after prolonged UVC post-treatment for all samples can therefore be directly related to the increased crosslinking degree in the photopolymer material.

Weight loss in ethyl acetate for different photopolymer materials displays the similar trend as in acetone (Fig. 6.). However, weight losses in ethyl acetate are significant if using printing ink or printing plate washing agent that contains ethyl acetate. Although the weight loss in ethyl acetate is not significant (between 1.1% and 1.7%) for samples treated with officially recommended duration of UVC post-treatments, when varying the UVC post-treatment duration, the partial dissolution of photopolymer materials in ethyl acetate should be monitored.

Weight loss in toluene was most expressed for all samples and therefore most indicative in this research. Observing Fig. 6.a, one can see that UVC post-treated samples of ACE Digital material show the increasing trend of weight loss in toluene. This points to the expressed compatibility of cohesion forces in the material and solubility parameters of toluene.

Since these changes in the material network occur on the surface (*Wolf, 2009, Yousif and Haddad, 2013*), they can therefore influence the reproduction quality in the long run, since the degradation by erosion of ACE Digital material surface caused by UVC post-treatments is obviously present.

Expressed decrease of weight loss in toluene for Digital MAX samples at prolonged UVC post-treatment (Fig. 6.b) points to the conclusion of both increased crosslinking degree and the positive changes in cohesion parameters in the material regardless of the incorporation of the oxygen in the surface with its presumably destructive influence. Compounds containing oxygen bonds are not causing the degradation of Digital MAX photopolymer material, they are rather incorporated in the crosslinked structure. If explaining this result in terms of the changes in γ and its components (Fig. 7.), one can conclude that Digital MAX material is the most stable in toluene due to its highest γ among three tested materials.

For Cosmolight QS samples, both γ^d and γ^p decrease after 10 minutes of UVC post-treatment (Fig. 7.) and cohesion parameters in the material therefore decrease, as well. This can be caused by both migration of the non-polar components to the surface of the material and

the simultaneous start of the bond breakage in the photopolymer network, resulting with the dissolution of segments in toluene and the increased weight loss (Fig. 6.c).

The relation between γ and material's resistivity to solvent is a valuable note when using particular solvent in ink/coating formulation and getting it in the contact with printing plate surface.

Finally, cohesion parameter of the photopolymer material itself is not an only indicator for printing plate's behavior in the contact with specific solvent: its (modified) surface properties will have a noticeable influence, as well.

Prolonged UVC post-treatment results with changes in the types and strengths of bonds in the surface layer of the photopolymer material used as a flexographic printing plate, pointing to the possible start of the surface degradation and/or migration processes.

In order to define the influence of the changes of weight loss in solvents (and therefore changes in crosslinking degree of the materials) on γ^d, Pearson product-moment correlation coefficient (measure of the linear correlation between two variables - r) for weight loss (Eq. 3) in different solvents and γ^d influenced by UVC post-treatment was calculated and displayed in Table 3.

$$r = \frac{\sum_{i=1}^{n}((x_i - \bar{x})(y_i - \bar{y}))}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2 \sum_{i=1}^{n}(y_i - \bar{y})^2}} ,$$

(3)

$\{x1, \dots x_n\}$ and $\{y1, \dots y_n\}$ present the datasets containing n values, while and   present the dataset means.

Table 3. presents the r values for weight losses in solvents and γ^d of printing plates exposed to varied UVC post-treatments. Changes in γ^d occurring with varied UVC post-treatment are strongly related to weight loss in all solvents for Digital MAX photopolymer material. γ^d of ACE Digital displays very good correlation with weight loss in ethyl acetate, but not in acetone and toluene. Cosmolight QS photopolymer material displays good negative correlation of γ^d and weight loss in acetone, but its solubility in other solvents is not directly related to its surface properties.

Table 3. Calculated r values for weight loss and γ^d of photopolymer materials for the set of samples exposed to varied UVC post-treatment

Weight loss (%)	γ^d (ACE Digital)	γ^d (Digital MAX)	γ^d (Cosmolight QS)
Acetone	-0.65	-0.96	-0.73
Ethyl Acetate	-0.95	-0.98	-0.46
Toluene	0.52	-0.95	-0.67

High r values can be interpreted as a direct connection between crosslinking degree, γ^d and solubility in specific solvent. Specifically, Digital MAX samples show excellent negative correlation of γ^d and weight loss in different solvents, pointing to the strong inversely proportional relation of these two values. This means that the increased γ^d of the material as a result of the increased crosslinking degree directly decreases the solubility in all used solvents. However, there is no valuable correlation for γ^d and weight loss in toluene for ACE Digital material. This is due to the fact that ACE Digital has the lowest γ^p and γ^{total} among tested photopolymer materials (Fig. 7.a - c). Its solubility in toluene which has highest dispersion forces compared to acetone and ethyl acetate (Table 2.) is obviously not dependent on the changes of surface properties. γ^d of Cosmolight QS samples displays the best correlation with the weight loss in acetone. Since Cosmolight QS material has the highest γ^p among tested printing plates (Fig. 7.c), its influence on the compatibility of the forces in acetone and Cosmolight QS is expressed.

It can be concluded that, depending on the type of photopolymer material, there is a direct negative correlation between γ^d and the weight loss caused by the immersion in the specific solvent. Strong negative correlation present for all used solvents establishes the direct relation between the crosslinking degree and the solubility parameters of the solvents. Furthermore, the solvent can interact with the photopolymer material independent of the changes of its surface structure after the UVC post-treatment and cause the partial dissolution of the photopolymer's soluble segments. Therefore, the influence of the solvents in the flexographic reproduction system, although adjustable by the post-treatment of the flexographic printing plate, needs to be carefully monitored in terms

of the printing plate's changed surface properties.

5. Conclusion

The aim of this paper was to establish the relation between the swelling properties of different photopolymer flexographic printing plates and the UVC-induced changes in their surface properties.

The results of the swelling experiments for three used solvents (acetone, ethyl acetate and toluene) displayed the highest normalized degree of swelling in toluene due to the highest dispersion forces in toluene compared to other used solvents. Furthermore, it was shown that tested photopolymer printing plates do not express the hydrogen bonding capability. Although the swelling in acetone and ethyl acetate were not significantly expressed, they point to the conclusion that the influence of the solvent on the photopolymer flexographic printing plates needs to be monitored in the graphic reproduction process in relation to the UVC post-treatment of the printing plate.

The weight loss after the immersion in solvents displayed the decreasing trend that can be directly related to the increased crosslinking degree in the sample, with the exception of the increasing trend for ACE Digital and Cosmolight QS samples. The analysis of the correlation coefficients for weight loss and γ^d, point to the conclusion that the interactions between the surface of the printing plate, as well as the initial compatibility of the printing plate cohesion parameters and the specific solvent's solubility parameters, are extremely important for several steps of the graphic reproduction process: the rinsing process, the adjustment of the duration of UV post-treatment and choosing the specific printing ink, as well as the washing agent after the printing process.

Considering observed it is possible to conclude that UVC radiation can be used as a tool for surface free energy customization of the polymer printing plates according to the specifics of every reproduction process in order to get a high quality print.

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