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Accelerated Aging of Photopolymeric Material Used in Flexography

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***Abstract*—**In this paper, a degradation of the photopolymeric material (PhPM), used as printing plate in the flexography reproduction technique, caused by accelerated aging has been observed. Since the basis process for production of printing plates from the PhPM is a radical cross-linking process caused by exposing to UV wavelengths, the assumption was that improper storage or irregular handling of the PhPM plate can change the surface and structure characteristics of the plates. Results have shown that the aging process causes degradation in the structure and changes in the surface of the PhPM printing plate.

***Keywords*—**Aging process, accelerated treatment, flexography, photopolymeric material (PhPM).

I. Introduction

FLEXOGRAPHY is a printing technique nowadays mostly used for the reproduction on packaging products and in printed electronics [1]-[3]. It is appointed by the usage of photopolymer printing plates produced and prepared in order to meet mechanical and qualitative requirements in the graphic reproduction process.

The basic role of the printing plate during the printing process is to transfer printing ink onto the printing substrate. Printing ink and/or other substances can be deposited on a variety of substrates (paper and non-paper substrates) and it is suitable for reproduction of labels, folding cartons, corrugated board and flexible packaging. Due to ability of PhPM printing plates to adsorb and transfer different types of printing inks to different substrates, it is applicable in functional printing as well. Functional printing involves the transfer of a printable substance to cause functionality such as a thermo-chromic reaction or control of conductivity on the substrate.

The application of the photopolymeric material (PhPM) used as a flexographic printing plate in reproduction systems was expanded in the last decade. Composition of PhPM ensures the stability of formed printing plate during the printing process, in the interaction with printing ink and substrate and in the re-printing processes as well. It contains different types of copolymers, most common styrene-butadiene-styrene (SBS) and styrene-isoprene-styrene (SIS) block copolymers, photo initiators sensitive to UV radiation, plasticizers which provide elastic properties, colorants and other additives. This kind of PhPM is used in industry and its reproduction properties and stability depends on many factors (i.e. composition of PhPM, printing plate production process, interaction with printing ink and the substrate, etc.).

In the last decade, a newly formed photopolymeric material (PhPM) has been introduced to the market for printing plates and a great improvement has been made in flexographic printing plate workflow. These facts have increased the quality of the printing plates overall and made the plate making workflow ecologically friendlier. Basically, workflow procedure is based on the effect of cross-linking process of certain organic compounds in the PhPM under the exposure of UVA and UVC radiation. When exposed to UV radiation, photoinitiator activates, double bonds in the structure break and the process of radical cross-linking occurs. The unexposed parts of the printing plate are then washed out in the processing solution [4]-[6]. Drying and post-exposure (UVA, UVC) follows and improve the mechanical properties of polymer material.

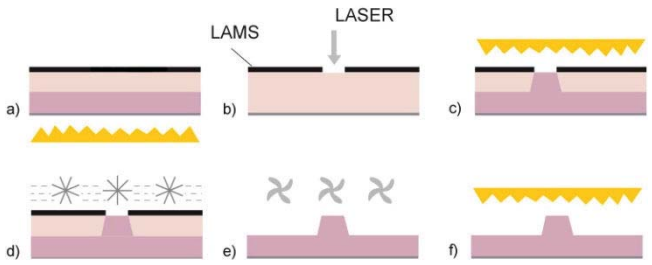

Fig. 1 Photopolymer printing plate workflow

Fig. 1 represents one of the most present printing plates making procedure [6], [7]. In the first step, UV exposure of the back side of the plate has been performed in order to form a basis layer (Fig. 1 (a)). Ablation of the LAMS (laser ablated mask) follows the back-exposure and forms a mask of the image which will be reproduced (Fig. 1 (b)). Printing elements have been formed by UV main-exposure through the LAMS mask in the PhPM (Fig. 1 (c)) and by chemical and mechanical developing non-exposed areas of the polymer are removed (Fig. 1 (d)). Drying and post-treatment (UVA, UVC exposures) improve the mechanical properties of the polymer printing plates (Figs. 1 (e), (f)).

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II. Experimental Settings

A. Hypothesis

In the graphic reproduction workflow, after the printing process, printing plates should be cleaned and usually are storage for the usage in the re-printing processes. Cleaning and the storage of the plates can, if there are not properly conducted, influence on the functional properties of the printing plates in the reproduction process. The assumption of this research was that improper storage or irregular handling of the PhPM plate can cause the degradation of the surface and structure of the printing plates. The study was conducted in order to evaluate the potential applicability of PhPM for printing process after a certain period of exposure to artificial weathering.

B. Preparation of Samples

The PhPM samples were produced according to the standard workflow conditions and prepared for the printing process [7]. Digital test image has been made in order to get measurable elements on printing plates (Fig. 2). It contained thin lines in positive and negative, raster elements and full tone areas.

Fig. 2 Digital test image (fragment)

Printing plates were exposed in weathering testing chamber Suntest XLS+ containing xenon lamps with high luminance and high color temperature, ranging from the UV to infrared irradiation. They were exposed up to 240 hours, which is the equivalent to one-year daylight exposure. The samples were tested periodically after a certain period of exposure. The PhPM samples were designated *S0* for non-aged sample, *S1* for sample aged 48 hours up to *S5* for sample aged 240 hours. Mechanical characteristics and chemical stability of accelerate aged PhPM samples and their reproducibility in re-printing process has been observed. Optical observation has been made in order to get a visual analysis of samples.

C. Measurement Methods and Devices

Mechanical properties of PhPM samples were measured by performing a hardness test. Hardness of the printing plate is a parameter that has to be defined and adjusted to the specific printing substrate and the reproduction system. It can be variable during the printing process and is connected to the elastic deformation of the PhPM. Softer the plate usually has more expressed deformation. Any kind of variations and changes in hardness of PhPM can cause the deformations in the printing process. Hardness test was performed by durometer Zwick Roell, Shore A range.

PhPM swelling was used for the estimation of the material's cross-linking and degradation. It was used in order to characterize changes in the ratio of polymerized compound in the material. Swelling can increase the volume of material due to absorption of a solvent. A highly cross-linked polymer shows less degree of swelling. Swelling measurements were performed by gravimetric method [8], in a controlled environment with a constant temperature of 25 °C. For swelling tests was used ethyl acetate (ACS grade). Ethyl acetate is usually used as a cleaning agent for removal of printing ink from the photopolymer plate after the printing process [9]. PhPM samples were immersed in the ethyl acetate for periods up to 120 minutes, after which the weighing showed that the equilibrium of swelling was reached. Normalized swell ratio (M_t) for control periods of 5, 15, 30, 60, 90 and 120 minutes of immersion were calculated using (1):

$$M_t = \frac{m_t - m_0}{m_0} .100\% \quad (1)$$

where m_t stands for the mass of the swollen polymer at a time t, and m_0 for the mass of the dry polymer sample before the immersion. After immersions, samples were dried at 80 °C by means of OHAUS MB 45 moisture analyzer, after which the solvent ratio in the sample decreased to 0.23% and stabilized. Samples were then weighted again to determinate the mass loss after the swelling.

The PhPM samples were analyzed by FTIR-ATR and EDS spectroscopy in order to define the changes in structure and composition of the PhPM. Samples were placed on a clean holder on the FTIR spectrometer Perkin Elmer Spectrum One, and the FTIR-ATR spectrum was analyzed by means of the program support.

EDS spectroscopy is a technique which works by detecting X-rays that are produced by a sample placed in an electron beam and analyzes the elemental composition of the sample. EDS was used in this paper to identify the ratio of carbon to oxygen in PhPM samples. After coating the samples with gold dust in order to make them responsive to the electron beam in the Quorum Technologies Sputter Coater SC7620, they were put in a TESCAN SEM VEGA TS 5136 MM Oxford Instruments Si(Li)EDS INCA 250 device. Program support gave the results of the carbon and oxygen mass portions in order to support the FTIR-ATR analysis and identify the influence of the accelerated aging on PhPM samples.

Microscopic images of testing elements on PhPM plates were made in order to determine changes of the lines and elements size by Olympus BX 51 microscope.

III. Results and Discussion

A. Hardness Test

Results of hardness test are presented in Table I. One can see that the initial value of 61.58 Shore A on sample *S0*

(PhPM without treatment) has increased due to the ageing process on 70.12 Shore A, sample *S5* (sample aged 240 hours).

TABLE I
RESULTS OF THE HARDNESS TEST

PhPM sample	*S0*	*S1*	*S2*	*S3*	*S4*	*S5*
Hardness (Shore A)	61.58	64.64	66.26	67.42	68.84	70.12

The hardness of the samples was increased by exposing to artificial light, probably due to the higher degree of cross-linking which results with a more compact PhPM structure.

B. Swelling Test

A swelling test was performed by the gravimetric method by using an ethyl acetate (ACS grade) as a swelling agent. Ethyl acetate has a regular application in flexography; it can be found in the composition of printing inks and as a solution for cleaning the ink from the photopolymer plate.

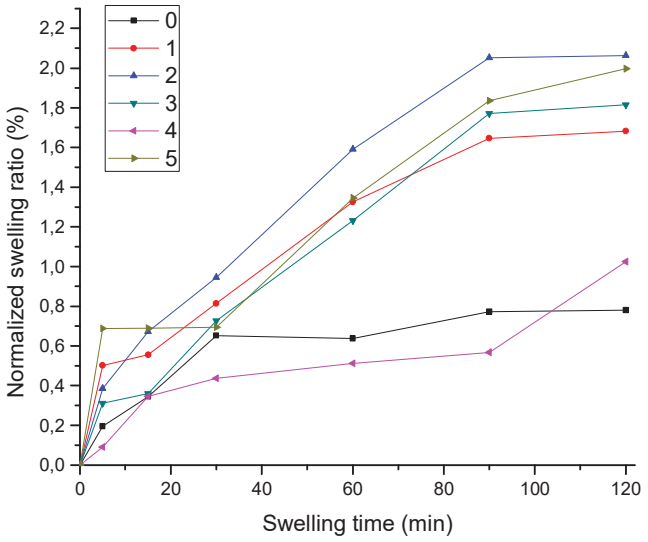

Fig. 3 Normalized degrees of swelling for aged PhPM samples immersed in ethyl acetate

In Fig. 3, one can see that ethyl acetate causes swelling of the PhPM used in the printing plate production. Generally, the degree of swelling of aged samples increases compared to the non-aged sample, reaching the equilibrium at approx. 120 minutes of immersion for all samples. Normalized degree of swelling in ethyl acetate reaches a maximum of 2.06 % with 96 hours of accelerated ageing. Variations of the swelling ratio of compared samples can be assigned to the changes in the type, and therefore strength of chemical bonds in the PhPM during the ageing process [10]. Specifically, for the period of ageing up to 96 hours, the swelling ratio increases, which could be the consequence of the increased dispersive and polar forces of surface free energy which occurs in the PhPM due to the UV-induced cross-linking [11]. After 96 hours of exposure to accelerated ageing, the swell ratio decreases, but generally remains higher than the one of the non-aged sample. This indicates that the cohesion parameter of tested photopolymer in relation to the solubility parameter of ethyl acetate (total Hildebrand parameter for ethyl acetate is 18.1 $MPa^{1/2}$, with hydrogen bonding capability of 7.2 $MPa^{1/2}$, Hansen's polar component of 5.3 $MPa^{1/2}$ and Hansen's dispersion component of 15.8 $MPa^{1/2}$ [12]) are most similar after 96 hours of accelerated ageing, causing more expressed swelling. Furthermore, Fig. 4 presents the weight losses after the immersion of samples in ethyl acetate for 120 minutes and drying. Results show the normalized degrees of photopolymer swelling in ethyl acetate depending on the aging process.

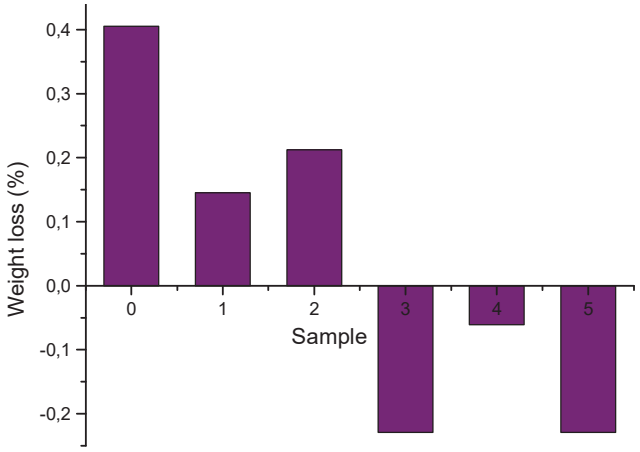

Fig. 4 Weight loss after swelling for aged PhPM samples immersed in ethyl acetate

One can see that the weight loss for *S0* has a highest value compared to the other samples. This indicates that the non-aged sample still has non-cross-linked compounds in its structure which will result with their dissolution in ethyl acetate. The period of exposure to accelerated ageing up to 96 (*S1* and *S2*) hours apparently causes cross-linking in the PhPM structure, therefore decreasing the ratio of dissolved portion in the swelling agent compared to *S0*. However, prolonged exposure to the ageing process (*S3* – *S5*) apparently causes the integration of ethyl acetate in the PhPM structure, since the weight loss after the drying process is negative. This could affect the PhPM's mechanical properties and the adsorption of the printing ink on its surface.

C. FTIR-ATR Spectroscopy

FTIR-ATR analysis of the PhMP aged in an artificial environment primarily displayed the changes in the area of oxygen-containing bonds. Results are shown in Fig. 5.

Changes in transmittance of FTIR-ATR spectra at 3200-3500 cm^{-1} and the peak around 1750 cm^{-1} point to the increased ratio of hydroxyl and carbonyl bonds in the PhPM, respectively [13]. The changes in the fingerprint area (below 1500 cm^{-1}) could not be defined due to the trade secret of PhPM plate's detailed composition, but could be generally assigned to changes in carbon-hydrogen and carbon-oxygen bonds [13].

Since the ratio of the bonds containing oxygen considerably increases with prolonged accelerated ageing, the surface properties of the PhPM are likely to change significantly, analogue to the changes caused by regular UV-treatments

[14]. Furthermore, since the oxygen has a destructive influence on the PhPM [15], accelerated ageing could cause its mechanical degradation during the exploitation process.

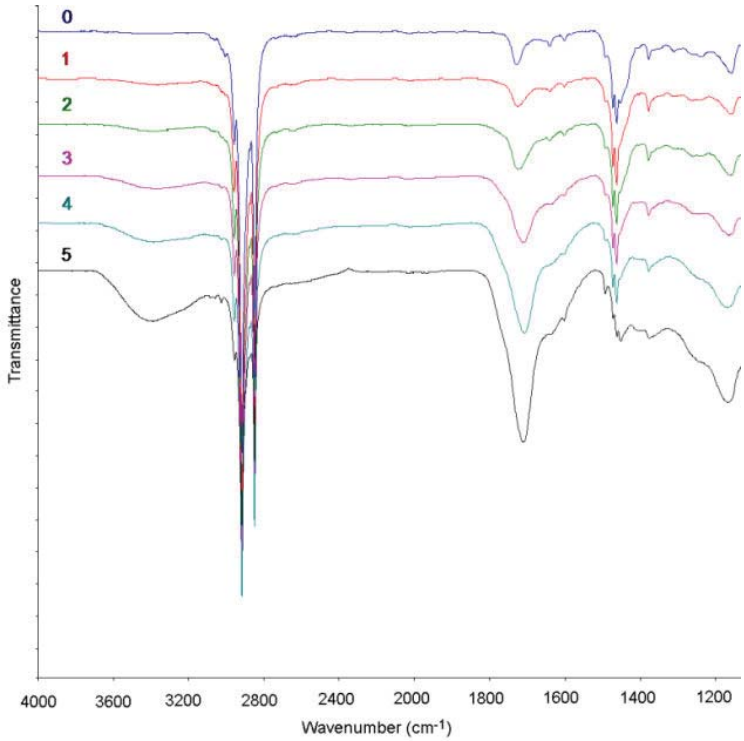

Fig. 5 FTIR-ATR analysis of PhPM samples of different aging period

D. EDS Spectroscopy

Results of the EDS show the ratio of oxygen in relation to carbon in PhPM samples and are presented in Table II.

TABLE II
RESULTS OF THE EDS SPECTROSCOPY

PhPM sample	*S0*	*S1*	*S3*	*S5*
O (%)	8.00	8.26	30.46	33.09

It is visible that the samples contain oxygen in different ratio. One can see that there has not been significant change between samples *S0* (newly prepared PhPM sample) and sample *S1* (PhPM sample aged 48 hours). Forty-eight hours of exposure to the artificial light is equivalent to storage of the printing plates of about 70 days in defined conditions. After 144 hours of exposure (*S3* PhPM sample) the amount of oxygen has been increased for almost four times (from 8.26% to 30.46%). Those results are in conformity with the results obtained by FTIR-ATR analysis and indicate that polarity of the PhPM surface has been increased, resulting in changes of the surface properties. It can cause deviations in the interaction of the printing plate with printing ink and substrate during the reproduction process and affect the mechanical properties of the printing plate in the exploitation process by decreasing its durability.

E. Microscopic Analysis

Microscopic analysis of the PhPM samples showed significant decrease of image elements caused by aging. Figs. 6 and 7 present images of formed printing elements on PhPM samples *S0* (non-aged sample, designated by (a) and *S5* PhPM sample aged 240 hours, designated by (b).

Microscopic images of PhPM samples gave results that correspond to the other analysis. In Fig. 6, one can see that rounded image element that presents 50% of surface coverage has a smaller coverage amount after the aging process. The coverage has been changed from 11805.19 μm^2 on the newly prepared sample (Fig. 6 (a) to 10095.62 μm^2 on the aged sample (Fig. 6 (b). Similar change has been detected on the line element formed on PhPM samples. Fig. 7 (a) shows an image of a line captured on a newly prepared sample *S0* and amounts 373.94 μm. Fig. 7 (b) shows a ticker line on aged sample *S5* and amounts 277.29 μm. Those microscopic images confirm the hypothesis that inappropriate storage of the PhPM samples cause damage and degradation of the PhPM printing plates. Furthermore, one can see in Fig. 6 (b) that certain cracks have been appeared between the rounded image elements in a form of irregular and sharp formed lines.

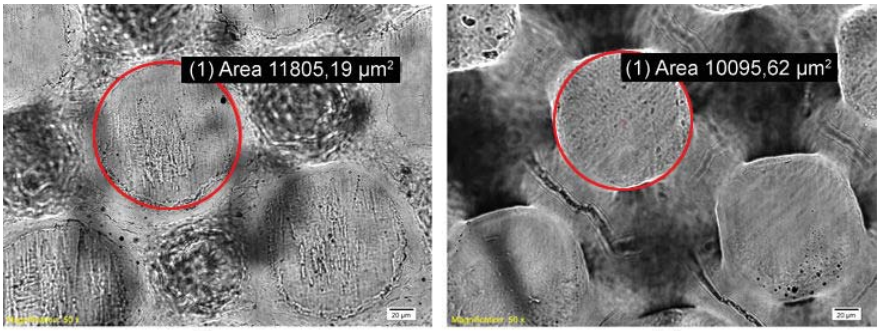

Fig. 6 Images of PhPM samples under magnification 50×

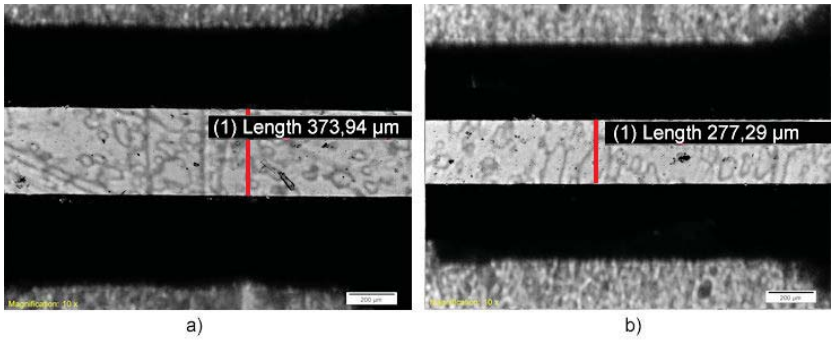

Fig. 7 Images of PhPM samples under magnification 10×

IV. Conclusion

This research was performed in order to define changes occurring in the PhPM used for flexographic printing plates after longer exposure to daylight (inappropriate handling and storage conditions). Different methods have been used for detecting and analyzing PhPM plates. The results obtained by different measurement and analysis methods lead to several conclusions:

- Hardness of the PhPM increases gradually, which can be assigned to the effect of UVA radiation present in the light source, which causes further cross-linking in the PhPM. Hardness increases for 8.52 on Shore A scale for the sample aged for a period corresponding to 1 year. This could result with decreased elasticity of the printing plate in the reproduction process and problems with printing on the rough printing substrates;
- Swelling experiments in ethyl acetate pointed to the inflexion point in the swelling ratio which reaches maximum with a sample aged for a period corresponding to 140 days. After that, swelling ratio decreases, but remains higher than for non-aged sample. This behavior is caused by the changes in the types of bonds in PhPM and needs to be considered when using ethyl acetate for the aged printing plate washing agent or in the printing ink composition;
- Weight loss after swelling decreased for samples improperly stored for up to 140 days. After that, changes in the surface and the bulk of the PhPM cause the permanent integration of ethyl acetate in the PhPM structure if put in contact. This could negatively affect both the mechanical and surface properties of the printing plate;
- FTIR-ATR analysis, together with EDS analysis, showed the significant increase of the oxygen amount in the PhPM, specifically in form of hydroxyl and carbonyl bonds. Since oxygen in higher portions (>30% after the exposure of the PhPM to inappropriate conditions for 210 days) could have a well-known destructive impact on polymeric materials, this could be an indication of the start of the degradation process.
- Microscopic images confirm the hypothesis that inappropriate storage of the PhPM samples cause damage and degradation of the PhPM printing plates.

Further research has to be directed to detecting the limits and consequences of the usage of aged and degraded PhPM printing plates in reproduction process.

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