論 文

Melted Photopolymer Composite Mass Transfer Effects during Flexographic Development*

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Abstract

This paper focuses on three separate processes of flexographic form development using DuPont FAST technology. These processes differ in terms of the volume, driving force, and absorption mechanism for low viscosity photopolymer into nonwoven materials. Research was conducted on the absorption capacity of nonwoven materials of different synthetic fibers. In addition, the possibility of using needle-punched nonwoven canvases, made from a mixture of synthetic and bicomponent fibers, to function as an absorbent of melted thermoplastic polymers in the production of print forms was also investigated. Geometric modeling shows that the amount of photopolymer extracted from the forming plates depends on the deformation experienced during compression, the plate dimensions, and the distance between the raster form printing elements. The optimal compression range of the forming plate and the thermal processing range of needle-punched nonwoven canvases for full extraction of photopolymer melt from the gaps in the printing forms were determined.

Keywords: Printing forms, flexography, nonwoven fabric, synthetic fibers, thermal processing, absorption, polymer melts, surface wetting, capillarity

Introduction

The new polygraphic method of making printing forms from photopolymerized plates using nonwoven materials is called “dry” or “thermal” production[1-3]. Producing printing forms without the use of organic solvents requires that materials have a certain heat resistance, thermal stability, surface activity, and absorption capacity.

The phase (capillary) mass transfer of liquid in the free space between the fibers forms the basis for the production of reinforced composite materials for structural purposes, intelligent textiles[4], electrically conductive fabrics and nonwoven fibrous materials[5], and pressure and tension sensors used in special clothing[6]. The phase mass transfer of a low-molecular-weight liquid in bodies formed by fibers has been studied by mathematical modeling methods[7], but this is not enough to describe and predict the process of absorbing a viscous melt into a non-woven material under pressure. The challenge of filling the fibers of material with liquid polymer during flexographic form application using DuPont FAST technology is due to the lack of excess absorbed liquid in contact with porous fiber materials and low contact time. These factors depend on the speed at which the material reaches the surface of the photopolymer plate, the curved forming cylinder, and the heated pressing roller[8]. Full removal of the liquid polymer from areas not meant to be colored and the areas between pixels requires knowledge of the relationship between the geometry, rheological properties, impregnating liquids, lyophilic behavior and fiber diameter, size and heterogeneity of the non-woven material’s porous structure, and the presence of an electrostatic charge on the synthetic fibers. The roll of large scale factors in the process of liquid absorption into porous materials without the use of excess liquid is researched in reference[9]. The results of theoretical studies of capillary strength and experimental measurements of the speed of mass transfer (absorbance) of water from a porous medium (glass) into a fibrous-porous medium (paper) show a dependence on pore size. If the pores in the fibrous-porous medium are much larger than the pores in the porous medium, which is partially filled with liquid, then no mass transfer of liquid into the fibrous-porous medium occurs. The liquid, acted upon by a small force, such as its own weight or hydrostatic pressure, fills only the voids of the first layer and flows in a radial direction. The direction and intensity of the mass transfer can be changed by

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changing the size of pores in the fibrous-porous medium. In order to strengthen the absorbent fibrous-porous material and reduce the pore size to the same level as the porous material, mass transfer of liquid between the contacting layers must increase.

The goal of this research is to develop a high quality explanation for the difficult process of mass transfer with limited liquid polymer volume between two porous mediums with short contact time. In addition, the applicability of current knowledge of phase type mass transfer of water in paper based materials to various stages of the flexographic form creation process using DuPont FAST technology is checked.

Materials and Methods

Non-woven materials were made from synthetic fibers:

- DuPont Cyrel DR37F
- Needle-punched non-woven material made from a 1:1 mixture of polypropylene fibers (PP) 0.67 tex and bicomponent polyethylene fibers (BCP) 0.44 tex;
- Needle-punched non-woven material made from a 1:1 mixture of polyethylene terephthalate fibers 0.33 tex and bicomponent polyethylene fibers 0.44 tex;
- Flexographic high strength photopolymer plates for the creation of forms by DuPont Cyrel thermal technology: DFR 045 635x762 mm and 1.14 mm thickness;
- DuPont FAST photopolymer: A mix of styrene-butadiene-styrene and styrene-isoprene-styrene copolymers with melt flow index (MFI) of 10.6 g/10 minutes at 140 °C and 2.16 kg piston mass.

The creation of the photopolymer plates, containing white areas and print elements filled with unpolarized photopolymers, was conducted using the following method. The black masking layer was removed from the DuPont Cyrel DFR 045 plate, and a negative image on the polyester film was placed on top of the photopolymer layer. Pre-irradiation with UV light was performed on the underside of the plate for 2 min using an Argon Tris exposure device. The main irradiation through the negative image of the sample was made from the front side for 10 min for photopolymerization (curing) of rasterized printing elements.

From the non-woven material used for the tests, a 40x40 mm square was cut and weighed. The photopolymer plate samples were placed on a refractory substrate in a heating chamber made by Binder GmbH at a temperature of 180-200 °C for 5 minutes. After thermal treatment, a non-woven material square was placed onto the photopolymer plate, and a 1 kg mass was used to apply pressure onto the non-woven material. The sample was placed under pressure for 1 minute. During this time, the polymer becomes heated to a viscous-flowing state and becomes absorbed into the contacting non-woven material square. Since the polymer passes from a viscous to a highly elastic state as it cools, it loses its ability to flow through the capillaries. Therefore, the sample was again placed in a heating chamber for 3 minutes before the layers were separated.

After reheating, the molten sample was separated from the nonwoven material. Mass transfer of the polymer into the porous structure of the fibrous materials was evaluated gravimetrically according to the technique described in reference[10)]. The increase in the weight of the nonwoven material and the decrease in the weight of the sample of the photopolymer plate were compared. By observing the increase in weight of the non-woven fabric squares or the weight loss of the samples of the photopolymer plates, a comparative evaluation of the absorbency was made. Using this information, the material most suitable for use in the DuPont Cyrel FAST technology can be selected. Scanning electron microscopy (SEM) images of the surface of flexographic plates produced by Toyobo Printight and Kodak Flexcel NX, obtained by solution technology, and flexographic forms obtained with DuPont FAST technology were made using a JEOL JSM-7500F SEM instrument. Modification of the structure of a non-woven fabric consisting of 50% polypropylene and 50% bicomponent polyethylene fibers was made by heat-pressing using an RDM HSE-3 laboratory heat-sealing machine. The optimal conditions for thermo-pressing of a non-woven material was selected based on previous research[11)]:

- Temperature of upper and lower pressing plates – 150 °C.
- Pressing pressure – 20 psi
- Pressing time – 20 s

An 8x10 cm sample was cut from a non-woven fabric, and a 100 μm anti-adhesive film of PTFE was laid on two sides. Then, the non-woven material was heat-treated using the heat-sealing machine operating using the previously stated optimal pressing conditions.

Results and discussion

Quantitative analysis of SEM images of flexographic forms intended for printing text as well as color background and various images on polymeric packaging materials allows concluding that the dimensions of large voids (gap elements) exceed 2 mm, and the intervals between printing elements (points) of rasterized images are 0.3-0.5 mm in **Fig.1**. After photopolymer plate UV irradiation, these cavities become filled with a liquid substance not participating in the photopolymerization reaction. The pore sizes in needle-punched nonwoven materials from a mixture of synthetic fibers are comparable to the gap sizes between the printing elements and are 0.2 to 0.4 mm, depending on the technique of forming the nonwoven web and the method of bonding the fibers[12)].

Spontaneous transfer of liquid (polymer melt) into the contacting nonwoven fabric with an average pore size of about 1 mm is possible only from the larger gap

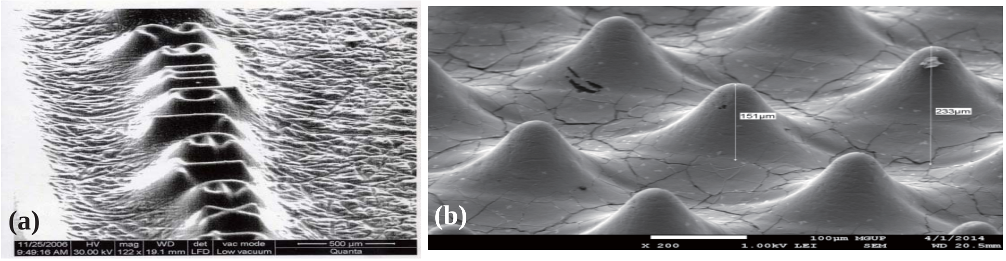

Fig.1 (a) Type of printing elements of a polymeric flexographic shape; (b) Micrograph of raster dots of printing elements obtained using the DuPont FAST technology.

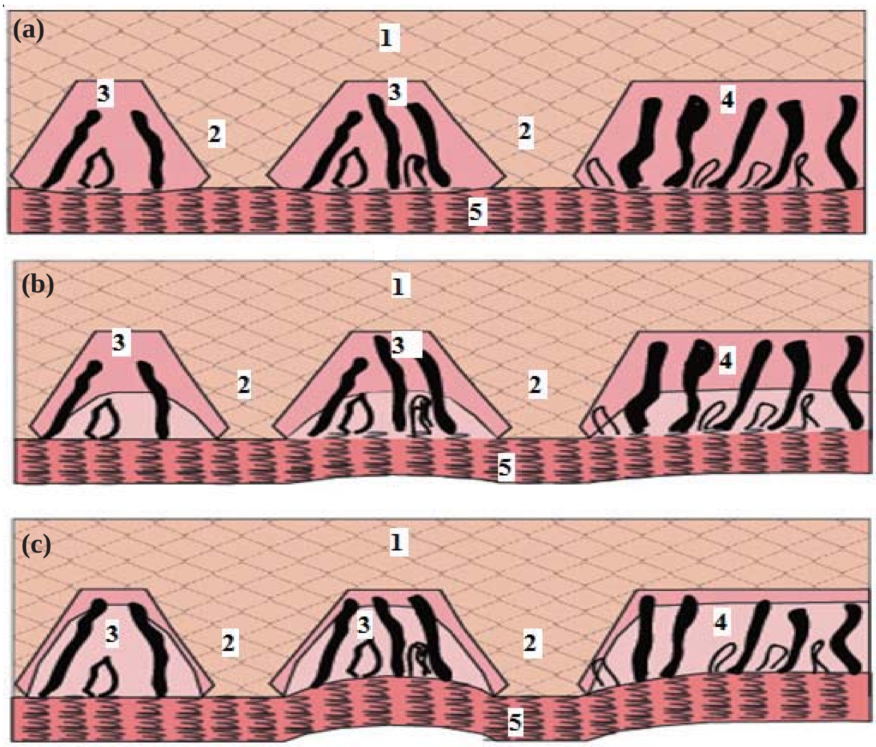

Fig.2 Schematic of successive stages of "development" of photopolymer forms by non-woven material using the DuPont FAST technology: (a) first contact; (b) intermediate contact; (c) the final contact, where: 1– flexographic form; 2 – printing elements of raster points; 3 – small spaces between printing elements of raster points; 4 – whitespace between the lines and letters; 5 – non-woven fabric.

elements of the flexo-form$^{6)}$. For a more complete removal of the liquid polymer from whitespace of less than 1 mm in size and the micro-space between the raster dots, it is necessary to seal the fibrous porous web with a goal to reduce the pore size, increase the external pressure on the elastic printing plate, and/or increase the wettability of the surface of the polymer fibers. The effectiveness of these technological methods is different at different stages of development of flexographic forms. The process of development of flexographic forms using the DuPont FAST technology by repeatedly pressing the fibrous-porous non-woven fabric to a heated preform can be divided into three characteristic stages in Fig.2.

In stage Fig.2(a), at first contact, the polymer melt is pressed into the porous structure of the web by the force of the pressure roller. Mass transfer at the stage (a) does not depend on the chemical composition of the fibers, their surface properties, or the dimensions of the porous structure of the web since mass transfer in this stage occurs through mechanical pressing of the melt into the gaps between the fibers.

In the intermediate stage in Fig.2(b), the interface between the phases of "photopolymer melt-fiber-forming polymer" is represented by the surface of the fibers as the "walls" of through pores and microscopic voids at the points of contact between the fibers. The pressure of the pressure roller of the "blotting" mechanism on the liquid melt of the photopolymer is absent since compressive deformation of the printing element is insufficient to squeeze out liquid from small whitespace areas. Mass transfer follows the characteristics of capillary absorption and depends on the wettability and diameter of the fibers, as well as the size of the microcapillaries between the polymer fibers.

At the finishing stage in **Fig.2(c)**, the interface between the phases of the "photopolymer melt-fiber-forming polymer" is extremely small and is apparently represented only by points of contact of individual ends and loops of fibers with the remaining liquid in the pores. Mass transfer in stage **Fig.2(c)** depends on the energy of intermolecular interaction (adhesion) at the phase interface of the "melt photopolymer composition-fiber-forming polymer", the adhesion energy and cohesion ratio of the photopolymer composition, as well as the possible electrostatic charge of the fibers.

For semi-quantitative analysis (evaluation) of the mass transfer intensity of liquid polymer at different stages of the process of "developing" photopolymer forms using non-woven material using the DuPont FAST technology, mathematical modeling methods are applied[13)]. To achieve the goals of this paper, we used a simplified geometric model of the rasterized flexographic printing plate (**Fig.3**) and a laboratory experiment simulating the process of absorbing the polymer melt into fibrous-porous non-woven materials of various degrees of compaction following the technique described in reference[10)].

As a geometric model, a group of four rectangular prisms having a height of 81 units of length separated by distances of either 5 or 9 units of length (**Fig.3**) were used to estimate the amount of the melt of the photopolymer composition "pressed" in stage **Fig.2(a)** into the non-woven fabric upon compression deformation of the preform of the flexographic printing plate (under the action of a heated roller). From the condition of constant prism volume with a decrease in height, the decrease in the volume of free space was calculated (**Table 1**).

The change in the shape of the printed elements of the geometric model as they compress was used to determine the volume of the polymer extruded from the blank spaces. Let the height of the printed elements in the undeformed blank of the printing plate be 81 units of length, and the distance between them 9.5 units, with a section of 1x1 units. Then the volume of liquid polymer in the gap between them will be 9x9 - 4x0.25 = 80 units. During thickening of printing elements due to compression to a cross-section of 2x2 units, their size decreases fourfold, which corresponds to a deformation of 75% (**Table 1**). At the same time 80x81 - 20x77 = 4920 units can be squeezed out of the workpiece, which is about 76% by volume. **Fig.3a** illustrates that after the plate is compressed to 25% of its original thickness, the amount of melt extruded from the raster structure with a separation distance of 9 units is more than 3 times more than the amount of melt squeezed out of the raster structure with a separation distance of 5 units.

Fig.3(b) shows the dependence of the extruded polymer melt volume on the relative deformation of compression of printing elements with a cross section of 1 mm^2, obtained with the help of a simplified geometric model of the preform of a flexographic mold. The dependence is linear, so we can state that the volume of the extruded polymer melt is proportional to the relative deformation of the compression. For an experimental evaluation of mass transfer acceleration of polymer from the micropores of the flexo-form to the nonwoven material through printing element compressive deformation using the pressure of the "heated roller", the printing elements were compressed using a stand providing isothermal conditions for mechanical testing[14)]. Compression was carried out at 170 °C, creating a load on the printing plate many times exceeding the possible forces created by the heated roller with nonwoven web pressing against

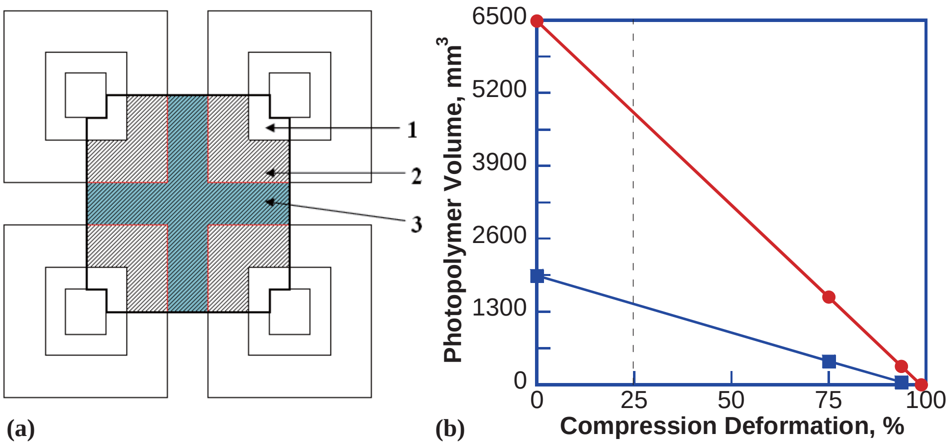

Fig.3 (a) Top view of the geometric model of the rasterized flexographic printing plate; (b) The dependence of the polymer melt volume on the relative deformation of the compression of the printing elements, where red line indicates 9 unit separation and blue line indicates 5 unit seperation. 1 - area of the section of the gap element before compression deformation; 2 - cross-sectional area of the gap element with compression deformation of 75%; 3 - the same for compression deformation of 94%.

Table 1 Deformation of printing elements of the model of a rasterized flexographic printing plate and the amount of free space between them.

The area of the section of the space element (S)	The volume (V) and the height (h) of the printing element	Relative compression strain ε $\varepsilon = (1- h_i/h_0)*100$, %	Volume photopolymer composition / fraction of melt yield under compression
The distance between the centers of the printing elements is 9 units			
S_1 = 9x9 - 4x0.25 = 80	V_1 = 1x1xh_1 = 81; h_1 = 81/1 = 81	0	6480/0
S_2 = 9x9 - 4x√2x√2/4 = 79	V_2 = 2xh_2 = 81; h_2 = 81/2 = 40,5	50	3200/51
S_3 = 9x9 - 4x1 = 77	V_3 = 2x2xh_3 = 81; h_3 = 81/4 = 20,25	75	1559/76
S_4 = 9x9 - 4x2x2 = 65	V_4 = 4x4xh_4 = 81; h_4 = 81/16 = 5,06	94	329/95
S_5 = 9x9 - 4x4.5x4.5 = 0	V_5 = 9x9x1 = 81; h_5 = 1	99	0/100
The distance between the centers of the printing elements is 5 units			
S_1 = 5x5 - 4x0.25 = 24	V_1 = 1x1xh_1 = 81; h_1 = 81/1 = 81	0	1945/0
S_2 = 5x5- 4x√2x√2/4 = 23	V_2 = 2xh_2 = 81; h_2 = 81/2 = 40.5	50	932/52
S_3 = 5x5 - 4x1 = 21	V_3 = 2x2xh_3 = 81; h_3 = 81/4 = 20.25	75	425/78
S_4 = 5x5 - 4x4 = 9	V_4 = 4x4xh_4 = 81; h_4 = 81/16 = 5.06	94	46/98

the forming cylinder during the development of the form[15] (Fig.4).

According to the compression diagram of the polymerized photoplate with the text (flexographic shape), it is seen that the "flexed" sections of the flexo form after UV irradiation are elastically (pseudoelastically) deformed and then destroyed at a load of 1.7 or 2.7 kN. The maximum deformation of printing elements at the moment of failure is 0.2-0.25 mm and does not exceed 25% of the thickness of the mold, which apparently provides only a partial extrusion of the photopolymer melt from the gap elements. This mass transfer is not enough to produce a high-quality shape with rasterized printing elements even after repeated cycles of blotting.

A laboratory experiment simulating the process of absorbing a polymer melt into fibrous porous nonwoven materials was carried out as described above[10] using a special absorbent material manufactured by DuPont, Cyrel DR37F and a domestic non-woven fabric from a mixture of 50% polypropylene (PP) fibers and 50% bicomponent polyethylene fibers (BCP) before and after sealing heat treatment. The mass transfer of the melt of the photopolymer composition from the mold into the porous structure of the fibrous materials was evaluated gravimetrically by increasing the weight of the contacting nonwoven material in Fig.5.

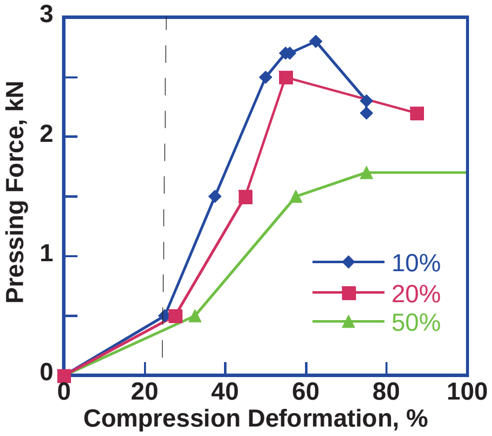

Fig.4 Compression diagram of the flexographic form of DuPont Cyrel DFR 045 (1.14 mm) with text and different percentage of white space area at 170 °C.

From the obtained results, presented in the form of

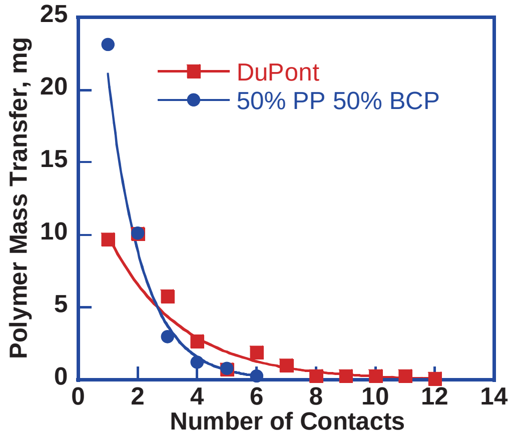

Fig.5 Mass transfer of the molten photopolymer composition from the flexographic shape, depending on the number of contacts with the nonwoven material. DuPont non-woven fabric and modified (heat-treated) non-woven fabric of 50% PP and 50% BCP fibers. Solid curves are exponential fits to the data.

graphs, it is seen that when a non-woven material is contacted with a heated flexographic blank a single time, a modified sample of 50% PP and 50% of the BCP absorbs twice more photopolymer melt in comparison with the DuPont Cyrel DR37F sample. After the non-woven material is contacted with a heated flexographic blank six times, the modified sample of 50% PP and 50% of BCP completely removes the melt. However, the DuPont Cyrel DR37F requires twelve contacts with the heated flexographic blank to completely remove the melt. This indicates that less contacts with the mold are needed to remove the melt of the non-polymerized photopolymer in the first stage of the development process.

The large ability of absorption of the photopolymer melt by the non-woven PP and BCP material mixture in comparison with the DuPont material is due to the fact that DuPont uses a polyamide or polyester nonwoven material with insufficient total pore volume. In addition, the geometry of capillaries between fibers does not ensure rapid absorption of the photopolymer melt at the second and third stages of flexographic form development. The thermodynamic affinity of the aliphatic fragments of the copolymers styrene-butadiene-styrene, styrene-isoprene-styrene, and polypropylene copolymers, as well as aromatic fragments of the copolymer macromolecules with fusible polyesters, from which the sheath of bicomponent fibers are made, enhance photopolymer melt absorption at the second and third stages of the flexographic form development.

Conclusions

The process of development of flexographic forms using DuPont FAST technology includes three stages of mass transfer of a molten photopolymer composition from a UV-irradiated billet into an absorbing nonwoven material: extrusion, capillary absorption and melt adsorption by the surface of the fibers. The driving force for the mass transfer of the molten photopolymer composition in the first stage, the melt extrusion step, is the pressing force of the heating roller of the developing DuPont device. By using the method of geometrical modeling of the process, it is shown that the amount of extruded melt of the photopolymer composition depends on compression deformation, the dimensions, and the distance between the printing elements of the raster form. Absorbent capacity of the absorbant nonwoven material should not be less than the volume of the melt squeezed out by 25% compression of the mold blank. The investigated non-woven materials of various types and the developing material of DuPont Cyrel DR37F have insufficient pore volume and do not provide complete extraction of the melt from the preform in a single application. A modified heat treated non-woven web of a mixture of polypropylene and bicomponent polyester fibers has a photopolymer melt absorption capacity that exceeds the capacity of the DuPont Cyrel DR37F by two times, which allows to intensify the first stage of the development of the printing plate.

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