Diffusion of Mineral Oil in Styrene-Butadiene Polymer Films

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ABSTRACT: Mineral oil diffusion in styrene-butadiene polymer films was investigated with a simple gravimetric sorption method. Over the selected range of temperatures and film thicknesses for which sorption tests were performed, the diffusion process is described in terms of Fick's third law. Polymer dissolution was found to compete with the diffusion process especially at high temperature. Possible interference due to dissolution on data generated using a gravimetric method, resulted in an estimation of apparent activation energy using diffusion coefficient set calculated with Crank's half-time relationship. The mineral oil diffusion activation energy was found to be relatively high compared with those of hydrocarbons diffusing in natural and synthesized rubbers or cross-linked polybutadiene as reported in the literature. The influence of polymer T_g, crosslinking density, and polarity on mineral oil ability to penetrate polymer film was evaluated in terms of percent weight increase over time. Maximum absorption after 60-min sorption time linearly correlates with mineral oil absorption rate for polymers prepared with different structures. This linear relationship suggests that diffusion of solvent in styrene-butadiene polymers reveals the macroscopic composition and structural polymer modification rather than local changes. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2886–2891, 2009

Key words: diffusion; mineral oil; styrene-butadiene polymers; coated paper; printability

INTRODUCTION

Coated paper printability properties in offset printing are a subject intensively and continuously investigated by the paper industry. It relates to the way ink sets at the paper surface. Ink setting at the surface of coated paper is mainly controlled by two processes: (1) capillary-driven absorption of ink components due to the pore distribution of the pigmented coating and (2) diffusion-driven absorption of ink components into the very thin polymer film areas binding pigment particles and present at the surface of coated paper.[1] Mineral oils are diluents of offset inks which can be considered as representative solvent[2,3] to study the diffusion mechanism of fluid ink into those thin polymer film areas. Coated paper offset printing performances like back trap mottling, ink piling and blanket build up have been correlated with ink solvent/styrene-butadiene polymer interactions.[1,4]

The goal of the present work is to study the mineral oil diffusion process in styrene-butadiene polymer films. The diffusion process was found to follow Fick's third law within the selected tempera-ture and thickness ranges. Diffusion coefficients and activation energy are calculated using Crank's half-time relationship. Polymer T_g, crosslinking density, and polarity were investigated for their relative influence on mineral oil absorption rate.

EXPERIMENTAL

The styrene-butadiene polymers investigated are described in Table I. Glass transition temperature (T_g), percent gel, and polarity of polymer used in paper coating are known to influence the final offset printing performance.[1,5] The selected ranges are representative of binders used in the coated paper industry. T_g is a measure of the mobility of the polymer chains. It was measured on a Mettler DSC apparatus with a temperature ramp of 10°C per minute. Percent gel describes the crosslinking density of the polymer. The amount of insoluble polymer after swelling and dissolution of a polymer sample in various solvents, here toluene, is expressed as percent of insoluble based on the initial sample weight before immersion in the solvent. Polarity defines polymer surface energy and is here arbitrarily defined as none, medium (mp) or high (hp) depending of the polymer composition. Monomers such as vinyl acids, hydroxyethylacrylate, acrylamide, and acrylonitrile are usually used in emulsion

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TABLE I
Latex Description and Properties

Latex	Description	T_g (°C)	Gel (%)	Polarity
SB1	Low T_g, high gel	4	89	None
SB2	High T_g, low gel	23	46	None
SB3	High T_g, high gel, mp	19	80	Medium
SB4	Low T_g, high gel	4	88	None
SB5	Low T_g, low gel	0	40	None
SB6	Low T_g, high gel, mp	2	83	Medium
SB7	Low T_g, high gel, hp	1	85	High

polymerization to impart polarity to the polymer.[5] The sorption test consisted of immersing polymer film sections of 3-cm diameter and of 0.1-mm thickness in mineral oil. Details are described in a previous work.[6] The mineral oil used was PKWF 2831 from Haltermann with a distillation cut boiling point range of 280–310°C and containing 20% of aromatics. To determine the relative amount of polymer dissolved after 6 h of immersion, mineral oil aliquots were analyzed for the presence of polymer fragments such as styrene and related oligomers by pyrolysis-gas chromatography spectrometry.

RESULTS AND DISCUSSION

Fick's third law

Percent weight change of the polymer film section was monitored over a 6-h immersion time period. Weight increase was recorded every 5 min. SB1, a typical carboxylated styrene-butadiene polymer, was used to investigate the mineral oil diffusion process in a styrene-butadiene polymer film. Figure 1 shows the corresponding curves for the sorption test made at room temperature (22.3°C), 35, 41.9, 46, 49.5, 61, 73, 86, and 110–111°C for a film thickness of 0.1 mm. From 22.3 up to 49.5°C, the equilibrium weight uptake is not reached after 6 h of immersion. The equilibrium is obtained after approximately 10 min at 61 and 73°C. The two absorption curves overlap
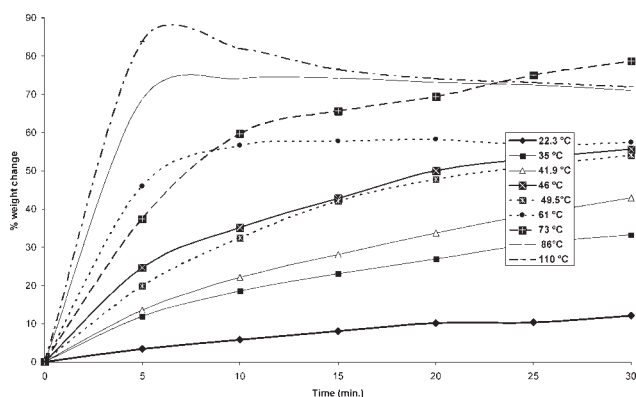
and are close to each other which indicates either a relatively similar diffusion process or else the inability of the test to differentiate between diffusion rate for a temperature change equal or below 10°C. This is true as well for temperatures of 46 and 49.5°C. At the higher temperatures of 86 and 110°C, very quickly a drop in weight is observed over time. It is interpreted as a concomitant dissolution overtaking the mineral oil diffusion as its reaches its equilibrium. After 6 h of immersion, the mineral oil aliquots were analyzed for the presence of polymer. Those aliquots were prepared with the same amount of mineral oil in which the film sections were immersed. Polymer presence in each aliquot was analyzed, after 6 h of immersion test, based on styrene amount identification by pyrolysis GC-FID technique. In Figure 2, styrene peak areas expressed as count (cts) are plotted against the temperature at which the sorption test was conducted. The analytical data confirm that polymer dissolution increases with the sorption test temperature.

To check which Fickian behavior mineral oil diffusion process follows, data of Figure 1 was processed as $M_t/M_{\text{sat}} = k\,t^{[1/2]}/z$ (with $k = 4/z\pi\sqrt{D}$) where M_t is the amount of solvent absorbed by the polymer at time t, M_{sat} is the equilibrium sorption amount of the solvent at infinite time, z the polymer section

Figure 1 Percent weight increase of SB1 film in mineral oil at different temperatures (film thickness 0.1 mm).
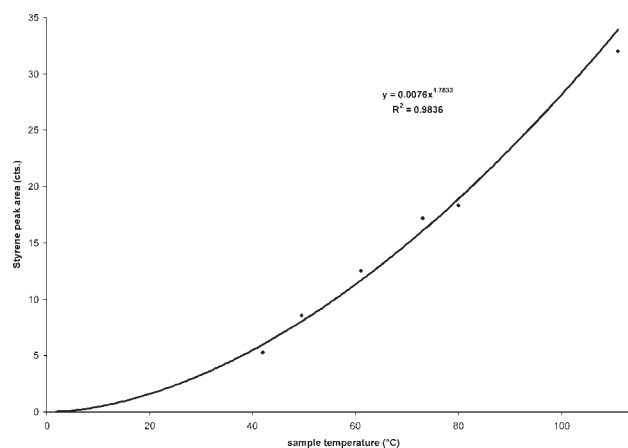

Figure 2 Surface area count (polymer content) for mineral oil aliquots after 6 h of immersion of SB1 film at different temperatures.
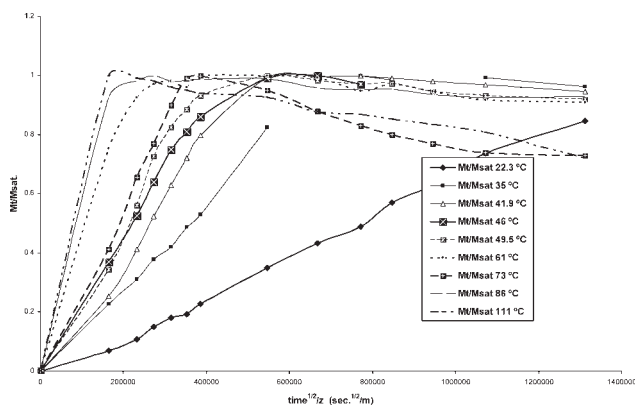
Figure 3 Fick's third law relationship for SB1 film in mineral oil at different temperatures.

thickness, and D the diffusion coefficient. The ratio M_t/M_{sat} shows a linear relationship with the square root of time followed by a plateau as seen in Figure 3. Even though one cannot ignore the dissolution process, the experimental data suggest that at all temperatures the mineral oil absorption process follows Fick's third law of diffusion.

Fick's third law assumes a diffusion process independent of the polymer swelling step taking place as the solvent penetrates the polymer. Deviations from this model are typical of crystalline phase containing polymers, of absorption process with an initial induction period and of diffusion into polymer below its glass transition temperature. This is not the case in this study or in conditions found during the printing process of coated paper.

Diffusion coefficient

Experimental data from Figure 3 was used to calculate diffusion coefficients. For the low temperature experiments where the equilibrium was not reached after 6 h of immersion, equilibrium uptake was tangentially extrapolated. For the experiments made at 86 and 110–111°C where dissolution is clearly taking place, the equilibrium uptake was taken as the maximum of M_t/M_{sat} seen during the sorption test just before the ratio starts to decrease due to polymer

dissolution. The diffusion coefficients were calculated with Crank's half-time relationship.[7] The half-time is estimated from the linear part of the curve $M_t/M_{sat} = k\ t^{[1/2]}/z$. This linear part was smoothened by linear regression for each graph of Figure 3. Table II contains the original data and the diffusion coefficients calculated with Crank's half-time (0.5) relationship:

$$D = 0.04919/\ (t/z^2)_{0.5} \qquad (1)$$

in which D is the diffusion coefficient, $t_{0.5}$ the half-time taken in the linear part of the curve $M_t/M_{sat} = k\ t^{[1/2]}$ and $z_{0.5}$ the thickness of the polymer section at the half-time $t_{0.5}$. Equation (1) is applicable when there is an excess of solvent, when the sorption process involves a relatively long experiment time and when diffusion coefficients are assumed to be concentration independent. In our experiments, an excess of mineral oil was used and the data generated correspond to a relatively long time frame compared with the printing process time. Such diffusion coefficients are relatively small compared with those reported in the literature[8] for diffusion of n-alkanes in various elastomeric polymer membranes.

Activation energy

With competitive polymer dissolution taking place especially for experiments conducted at elevated temperature, only an apparent activation energy is estimated. The fact that the slope of the linear part of the graphs of Figure 3 increases regularly with the experiment temperature is an indication for the diffusion process to first dominate before dissolution takes place. If dissolution was faster than diffusion at high temperature, the slope of the corresponding Fick's law relationship would be significantly affected. In Figure 4, the slope of the linear part of Fick's relationship graphs (in Fig. 3) is plotted against experiment temperature. At 86 and 110–111°C, this slope starts to level off indicating polymer dissolution begins to overtake the diffusion process. Figure 4 trend indicates that diffusion is still

TABLE II
Diffusion Coefficients

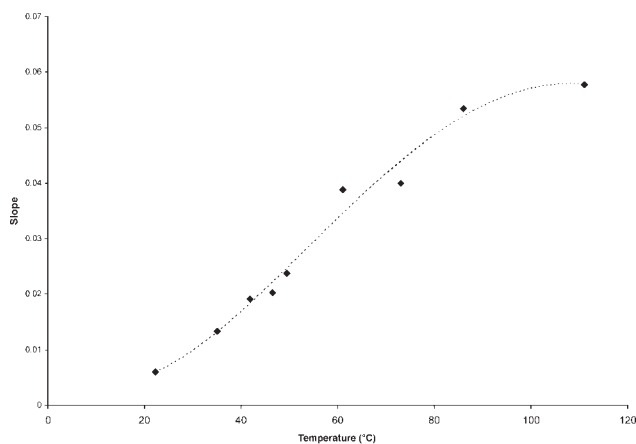| Temp. of sorption test (°C)	$t_{0.5}$ (s)	$z_{0.5} \times 10^{-5}$ (m)	$z^2_{0.5} \times 10^{-8}$ (m)	D (m²/s)
22.3	10800	11	1.21	5.53E^{-14}
35	3600	11.4	1.3	1.78E^{-13}
41.9	3600	10.5	1.103	1.51E^{-13}
46.5	2700	13.1	1.71	3.14E^{-13}
49.5	1800	9.55	9.025	2.47E^{-13}
61	1800	10	1	2.74E^{-13}
73	756	10.5	1.103	7.2E^{-13}
86	450	9.55	9.12	1E^{-12}
111	150	8.35	6.972	2.29E^{-12}

Figure 4 Slope of the linear part of Fick's third law relationship for SB1 film (from Fig. 3) at different temperatures as a function of experiment temperature.

TABLE III
Percent Increase in Surface due to Section Thickness

Section thickness (mm)	Section diameter (cm)	Surface of section thickness $\times$ 10^{-4} (m^2)	Surface ratio faces/ thickness	Surface increase due to thickness (%)
0.1	3	0.0942	150	0.67
0.2	3	0.1884	75	1.33
1	3	0.942	15	6.67
2	3	1.884	7.5	13.33

the dominant process at least during the first instant of sample immersion at 86 and 110–111°C. This is confirmed by the fact that when plotting Log D versus 1/RT for activation energy determination a linear relationship is obtained even with the 86 and 110–111°C experiment data. Therefore, dissolution was ignored in the early diffusion phase as a first approximation for activation energy calculation.

The activation energy E_d was calculated using the simple Arrhenius equation: $D = D_{0e}^{-(E_d/RT)}$. E_d is the slope of the curve Log D = Log D_0 − (E_d/RT). Plotting Log D versus $1/RT$ gives an activation energy of 37.16 KJ/mole and a D_0 of 2.6E-07 m^2/s. This is a high energy barrier for a diffusion process.[8,9] Studies investigating solvent transport in different polymer types usually indicate activation energy in the range from 2 to 25 KJ/mole. A value of 33 KJ/mole has been reported by Harogoppad and Aminabhavi[9] for the diffusion of nonane in neoprene. The high activation energy value obtained in our study could be explained by two factors: the high molecular weight of the solvent—mineral oil—and to a less extend, the drift due to the temperature dependant polymer dissolution as the mineral oil penetrates the film.

Film thickness

To simulate offset ink mineral oil absorption into polymer film found in coated paper, experiment on as thin as possible film sections is of peculiar interest. The thickness of polymer film areas binding pigment particles and found at the surface of coated paper is estimated[6] to be approximately 1.4 μ. Film thickness was investigated with the polymer SB1. The thinnest homogeneous film that could be produced was 0.1 mm. It is generally assumed[10] that solvent diffuses first perpendicular to the sample

surface until its reaches the center of the sample and starts diffusing horizontally. For high film thickness, the diffusion process might be different as the film section thickness contribution to the surface offered to the solvent cannot be neglected anymore. The thicknesses investigated in this study goes from 0.1 to 2 mm with a constant diameter of 3 cm (surface of faces is 14.13 10^{-4} m^2). The percent surface increase due to the film thickness is calculated in Table III.

The time dependant plots of percent weight increase and percent weight increase per unit surface which takes into account the thickness surface lead to similar graphs. During the sorption test, the swelling of the section is more important at smaller thicknesses than at higher ones. Both observations support the hypothesis that thickness effect can be neglected as a first approximation. Figure 5 confirms that at a constant temperature of 35°C for different film thicknesses, mineral oil sorption in SB1 film follows Fick's third law.

Influence of polymer structure and composition

Polymer chain mobility (T_g), crosslink density [expressed as percent (%) gel] and polarity were investigated. The legends of Figures 6 and 7 contain after the polymer reference the corresponding T_g
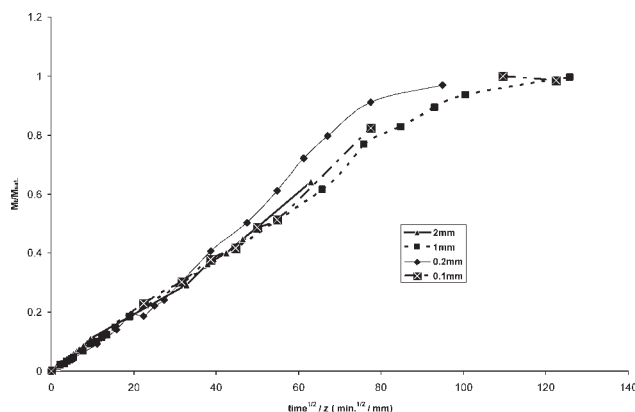

Figure 5 Fick's third law relationship for SB1 film in mineral oil of different thicknesses at 35°C.
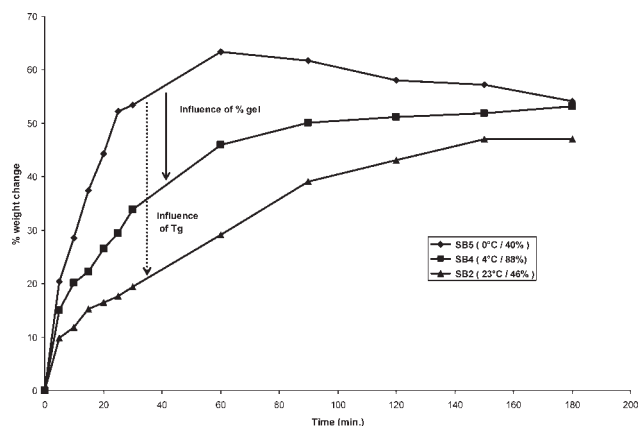
Figure 6 Influence of polymer T_g and crosslinking on mineral oil sorption.

Figure 7 Influence of polymer polarity on mineral oil sorption.

and percent gel. Figure 6 reports the relative influence of T_g and percent gel on the polymer film percent increase in weight as a function of time. In the range of crosslinking and T_g studied, T_g has a more pronounced effect on mineral oil diffusion than percent gel. This unexpected higher effect of T_g compared with percent gel is a strong indication of the importance of the polymer chain and inter crosslink segment mobility in the solvent diffusion process.

Polymer polarity has long been recognized as influencing ink solvent sorption.[1,11] Polarity seems to be the most important polymer modification affecting mineral oil diffusion (Fig. 7). The polymer polarity influence is attributed to the increase in solubility parameter difference between the polymer and the mineral oil.[1,6,11]

Maximum swelling and absorption rate

A polymer with an open structure (low crosslinking density) and high chain mobility (low T_g) has a faster mineral oil absorption rate. It should be expected as well to have a higher solvent absorption amount at equilibrium compared with highly crosslinked and rigid structure. Twenty different styrene-butadiene polymers including SB1 to SB5 were tested for mineral oil sorption. Some of the latices were synthesized with different polarity level, different T_g and/or different crosslink density phases within the same polymer by sequencing the composition of monomers.

T_g and percent gel range cover a window of respectively, -15 to $35°C$ and 40, 60, 70 up to 90%. The presence of domains in polymers prepared with composition sequencing was confirmed by the identification of more than one T_g from dynamic scanning spectroscopy measurements. The maximum mineral oil absorbed by the polymer film is reached within the first 5 min for high absorbency polymer structure, after 60 min for most of the polymer films
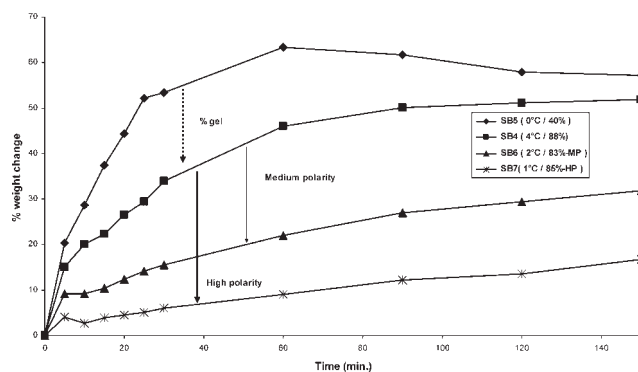
and within a much longer time for low absorbency polymer. The percent weight increase after 60 min of mineral oil was therefore selected as the best indicator for maximum mineral oil absorbency. After a longer time period, polymer dissolution may start to interfere too much with the diffusion process. Mineral sorption rate in Figure 8 abscissa correspond to the slope of the linear part of the graphs of percent weight increase versus time for all the twenty tested polymers. This measures the amount in g of absorbed mineral oil per minute per unit weight of polymer. In most of the cases, it is best evaluated after twenty minutes of immersion in mineral oil. Figure 8 shows a direct correlation between the rate at which mineral oil penetrates the polymer film and the corresponding solvent amount absorbed by the polymer after 60 min. Polymer structures that absorbed the mineral oil faster are the same ones that absorb more mineral oil at equilibrium. There is no deviation from this behavior nor is there a step change in diffusion process for the polymers prepared with different polarity, chain mobility and crosslinking density sequencing. The polymer
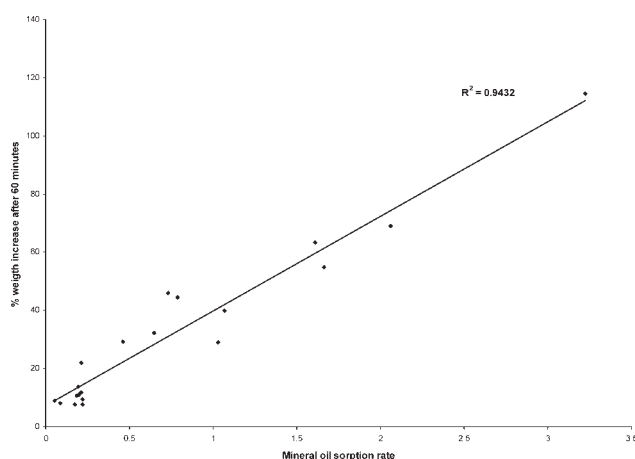

Figure 8 Mineral oil amount absorbed after 60 min as a function of mineral oil absorption rate.

structure description revealed by solvent diffusion experiments is the macroscopic polymer properties and is not related to the local polymer domain structures. Previous investigation on crosslinked polybutadiene[12] has underscored the primary influence of crosslinking density over the nature of the crosslink on solvent diffusion.

CONCLUSIONS

Mineral oil used as diluents in offset ink formulation can be used to study polymer film absorbency and model ink-binder interaction and its impact on coated paper printability properties. The present study is to describe and analyze mineral oil diffusion in very thin polymer films with a simple gravimetric test. The diffusion process was found to follow Fick's third law in the selected range of temperature and thickness. Diffusion coefficient and activation energy could be calculated although polymer dissolution starts to compete with pure diffusion process as temperature increases. The values obtained indicate a slow diffusion process. An investigation into polymer structure and chemical modifications revealed that the mineral oil sorption is influenced in order of importance by polymer polarity, T_g, and crosslink density. Experimental data from styrene-butadiene polymers prepared over a wide range of polarity, T_g, crosslink density, and composition sequencing support the conclusion[12] that mineral oil diffusion reveals overall polymer macroscopic behavior rather than local domain structural modifications.

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