Methylene Blue Adsorption From Aqueous Solutions to Flexible Poly(vinyl chloride) Silica Composites

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Methylene blue (MB) adsorption studies were performed with poly(vinyl chloride)-(dioctyl phthalate)-silica composites, which were obtained by using plastisol-plastigel technology. The films were flexible, having elastic modulus of 1.0–1.5 GPa. Diminishing MB concentration in the aqueous phase was followed as the adsorption process advanced by using visible spectroscopy. Contributions of the individual components of the composites to adsorption were also investigated. Although the MB adsorption capacity was extensively high for silica, it was moderate for the composite, most likely owing to the occlusion of pores of silica by plasticizer to some extent. The improvement of MB adsorption capacity of the composites as the silica ratio increased was explicitly deduced from the optical microscopy photographs. The diffusion coefficients of MB through the composites were 5×10^{-13}, 6×10^{-13}, and 3×10^{-13} m^2 s^{-1} with regression coefficients of 0.73, 0.89, and 0.88 for 0, 2, and 16% silica-containing composites, respectively. Because of the slow diffusion of MB in poly(vinyl chloride)-silica composites, using them as dynamic column adsorbent was not practical. However, these versatile plastics can be used as plastic labels, colored clothing, leather substitutes, antimicrobial medical devices, and laser printable surfaces. J. VINYL ADDIT. TECHNOL., 21:42–50, 2015. © 2014 Society of Plastics Engineers

INTRODUCTION

Microporous materials are obtained by the incorporation of silica particles into poly(vinyl chloride) (PVC) matrices [1]. Battery separators [2], ear tags [3], and column packing for the purification of proteins [4] are some of the application areas of such composite sheets. PVC composites are widely used in the production of leather substitutes as well [5–7].

The removal of a vast variety of contaminants from aqueous systems is of environmental importance, particularly for the removal of highly colored wastes of pulp and paper, and for the textile industry, which causes water pollution. Polymeric adsorption resins offer a great removal potential. Browne and Cohen [8] stated that once an appropriate polymer is identified as a desired candidate, then one can proceed with the second stage of resin design for optimal capacity, structural integrity, and pore size distribution [8]. They worked on the development of such a polymeric adsorption resin of polymer-grafted silica. Dye adsorption studies were performed from the environmental point of view by Karadag et al. [9] on hydrogels and by McKay [10] onto silica. McKay [10] reported the adsorption of Astrozon blue on Sorbsil silica fitted to a two-resistance mass transfer model. Adsorption on different silica types, such as MCM-41 [11], silica aerogels [12], and MCM-41, MCM-48, and MCM-58 [13], nanoporous SBA-3 [14], and diatomaceous silica [15], were studied in the literature. Reidlich-Peterson isotherm [11], Langmuir, and Freunlich isotherm [12, 14, 15] models were fitted to experimental data. The monolayer capacity on silica was reported as 116.5–300 mg/g [11–15]. Adsorption of methylene blue (MB) on PVC-zeolite composites were studied by Balköse et al. [16].

Dyeability is needed to render a plastic possible to scribe with water-based inks on plastic sheets. Karolyi [3] prepared 5 to 40% silica containing PVC sheets that are used as the ownership ear tags for animals. Maisel [17] showed that the addition of 1.5 phr of silica (Zeo 49) to PVC/(dioctyl phthalate) (DOP) formulations reduced the plate-out of Watchung red B by about 24%.

Silica is a very good adsorbent for MB, but because of its small particle size, it forms a colloidal dispersion in water. Fixing silica particles in plastic matrix eliminates their transfer to water. However, its adsorption capacity was reduced and rate of adsorption was slowed when it was encapsulated in the plastic matrix. On the other hand, it imparts dyeability to the plastic.

Silica can be dispersed in PVC by using different techniques. It could be dispersed in vinyl chloride prior to suspension polymerization. PVC grains with higher porosity were obtained and the distribution in the grains was

not uniform [18]. Another method is to use the organic/inorganic hybrids in which silica was produced in situ from tetraethoxysilane via a hydrolytic sol-gel processing route [19]. The transparent sols of silica in PVC plastisol were gelled by heating after vacuum application. The hybrid films containing 0–20% silica had spherical silica particles with 2- to 3-μm diameters [19].

MB can be introduced to PVC during solvent casting [20] or by swelling PVC products in solvents having MB [21]. A thin film coating was obtained by solvent casting from cyclohexanone solution containing PVC, sensitizer, MB, complexing agent, and a solvent [20]. PVC doped with complexed MB was used to record the incident light pattern in the polymer and it produced very legible letters with good contrast [20]. MB and gold nanoparticles were introduced in PVC catheters by swelling them in MB solution in water acetone and then shrinking in water for antimicrobial purposes [21].

To summarize, improvement of dye adsorptivity is of importance for dye adsorption from aqueous solutions [16], dyeability of plastics [3], printing on plastics [20], keeping the colors of printed material on plastics during processing [17], severe outdoor conditions [3], creating laser printable polymer surfaces [20], and making antimicrobial catheters [21].

The main purpose of the present study was to incorporate the adsorption capacity of silica into a plastic matrix in order to obtain a system that has a high capacity for dye adsorption and is convenient to use in column applications [4] as stacked or pelletized. Using such PVC-silica composite sheets as column packing, the packing time will be reduced and the surface available for diffusion will be increased [4]. Therefore, MB adsorption on flexible PVC-silica composites from aqueous solutions was investigated in the present study. Flexible PVC-silica composites having a porous structure were produced by using plastisol-plastigel technology. While equilibrium uptake evaluations were performed through visible spectroscopy and optical microphotography studies, a kinetic study was performed for the MB adsorption of composites as well.

MATERIALS AND METHODS

Materials

PVC powder (Petvinyl P 38/74 from PETKIM) having a density of 1.39 g/cm^3 and composed of spheres of a large particles ranging between 100 nm and 20 μm was used in the experiments. The specific surface area of the PVC powder was 16 m^2/g [22]. Precipitated silica, Zeo49 (Huber Corporation), was used in preparing the composites. The average particle size, the density, the surface area, and the pore volume of silica were reported to be 9 μm, 1.58 g cm^{-3}, 148 m^2 g^{-1}, and 0.12 cm^3 g^{-1}, respectively [23].

Silica Characterization

The surface area of silica was determined through N$_2$ adsorption at $-196°C$ by using a Micromeritics ASAP 2000 analyzer.

Selectivity Test of Silica to DOP or Water. One gram of silica powder was mixed with 10 cm^3 of DOP and 10 cm^3 of water at 25°C for 15 min at 400 rpm by using a magnetic stirrer. The mixture was kept for 24 h to separate the phases. The floating DOP phase over water was removed by using a pipette. The silica particles in the aqueous phase were separated by filtering the mixture thorough blue band filter paper. The wet solid phase was dried at 150°C for complete water evaporation. The masses of wet and dried solids were recorded. The transmission infrared (IR) spectrum of the dried solid was taken by KBr disk technique by using a Shimadzu IR-470 spectrophotometer.

Composite Preparation. One hundred grams of PVC was mixed with 60 g of DOP (Sankim Co., Turkey), 5 g of epoxidized soybean oil (EPSO; Akdeniz Kimya Co., Turkey), 2.75 g of calcium stearate, and 0.275 g of zinc stearate (CaSt$_2$ and ZnSt$_2$; Merck, Germany) to obtain a homogeneous plastisol by stirring at 200 rpm in a laboratory-type dough kneader (Rowenta). Small aliquots of the plastisol were mixed with 2, 4, 8, 12, and 16% in mass silica powder (Zeo 49; Huber Corp.), in a porcelain mortar with a porcelain handle.

The homogeneous compounds with and without silica were then deaerated under vacuum at room temperature at least for 2 h to eliminate the entrapped air.

Film Preparation. Gelation of the above plastisols with and without silica at $140 \pm 2°C$ for 16 min, between A316 stainless steel plates under 5 MPa of pressure in a hot press, led to the formation of plastic films of 314- to 560-μm film thickness. After cooling to 40°C, the films were taken out of the press.

Morphology of the Powders and the Films. The microphotographs of the gold-coated PVC powder and silica were obtained by using a Philips XL 30 S FEG and QUANTA 250F scanning electron microscope (SEM), respectively. Film morphology was determined by taking SEM microphotographs of the fracture surfaces obtained after immersing the samples in liquid nitrogen. QUANTA 250F SEM was used for this purpose after coating the surfaces with gold.

Density Measurements. Density of the films was measured by using water in a glass pycnometer.

Water Sorption. Strips of films were immersed in pure water for 2 weeks and weighed after removing them from water and blotting with tissue paper.

Differential Scanning Calorimetry (DSC) study. DSC measurements of stearates and composite samples were carried out by heating from 25°C to 160°C with a heating rate of 10°C/min, employing a Setaram DSC 92 analyzer.

Tensile Tests. Stress-strain diagrams of the (dog bone)-shaped cut samples were obtained by drawing samples at

a crosshead speed of 5 cm/min in an Instron 1026 tensile tester.

MB Uptake of the Films. Composite films were equilibrated with 0.04 g dm^{-3} of MB solution. A high concentration of MB was chosen to ensure complete coverage of the adsorption sites with MB. The visible spectra of MB adsorbed films were taken by using the transmission technique in a PerkinElmer 3 UV-visible spectrophotometer. The microphotographs of the films were taken with the transmission technique, using an Olympus CH40 microscope.

Sample Preparation for Adsorption Study. From the films, pellets with a 6-mm diameter were cut out by using a paper perforator for adsorption equilibrium and rate experiments.

Adsorption Isotherm Measurement. Equilibrium uptakes from 0.018 g dm^{-3} of MB solution by PVC composites without silica and with 16% silica, PVC, and silica powders were determined at 25°C, measuring MB solution concentrations by using a Jasco 7800 UV-Vis spectrophotometer. All MB-containing solutions were kept in the dark to prevent damage from sunlight.

Adsorption Rate Experiment. One PVC composite pellet having either 0, 2, or 16% silica was immersed in 5 cm^3 of 0.018 g dm^{-3} of MB solution. Aliquots measuring 1.5 nm^3 were taken at different time intervals and their MB concentrations were measured by using a NanoDrop 2000 UV-Vis spectrophotometer.

RESULTS AND DISCUSSION

Silica and PVC Powder Characterization

The Langmuir surface area of silica was determined to be 119 m^2/g from nitrogen adsorption isotherm at −196°C and the micropore volume was 0.0006 cm^3/g. The Barrett-Joyner-Halenda (BJH) adsorption and desorption pore volumes for the pores having a diameter between 0.300 and 1.7 μm were 0.081 and 0.084 cm^3/g, respectively. BJH adsorption and desorption pore diameters were determined as 6.83 and 6.52 nm, respectively. The properties of silica were found to be similar to the ones reported previously [23].

Silica particles of 20–30 nm were agglomerated to give larger particles as determined by SEM. The PVC particles had a broad particle size distribution between 100 nm and 20 μm [22]. The average diameter of the PVC particles was found as 525 nm from its 16 m^2/g surface area [22].

Gelation of the Plastisols

Silica particles were introduced in plastisols by mechanical mixing before the gelation process, which is
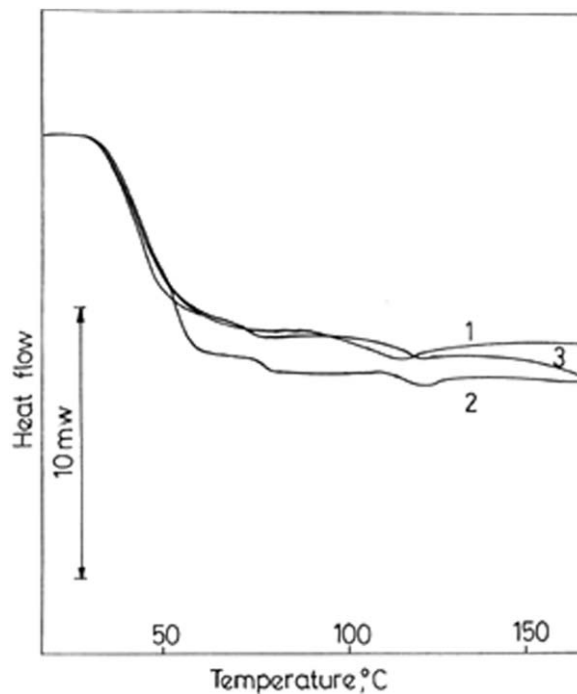

FIG. 1. DSC curves of composites having (1) 0%, (2) 8%, (3) 16% silica.

an easier processing method than introducing silica in the polymerization step of PVC [18] and synthesis of silica during gelation of silica [19].

PVC plastisols with and without silica are gelled by swelling of PVC particles with the plasticizer, fusion, and crosslinking of the swollen particles to each other during heating. In fact, it is low for gelation; a temperature of 140°C was chosen considering the low thermal stability of the PVC. At higher temperatures, PVC was dehydrochlorinated and darkened in color under the present conditions.

Film Characterization

Flexible films containing silica were obtained by gelling plastisol silica mixtures in a hot press under pressure. PVC, CaSt$_2$, and ZnSt$_2$ were first mixed in DOP and EPSO at room temperature to give a homogeneous distribution in plastisol and then they were melted at a film preparation temperature of 140°C. However, CaSt$_2$ and ZnSt$_2$ were recrystallized in the system upon cooling to 25°C as implied from their melting endotherm at 130°C [23] in DSC curves (Fig. 1). A glass transition temperature seen at about 80°C meant there were some PVC particles that were not completely dissolved by DOP.

All the films consist of a matrix of PVC dissolved in DOP and EPSO and dispersed phases of silica, CaSt$_2$, and ZnSt$_2$. DOP and EPSO were adsorbed by silica particles. As seen in micrographs of the fracture surfaces of the films in Fig. 2, silica was dispersed as large-sized agglomerates rather than as nanoparticles. However, the
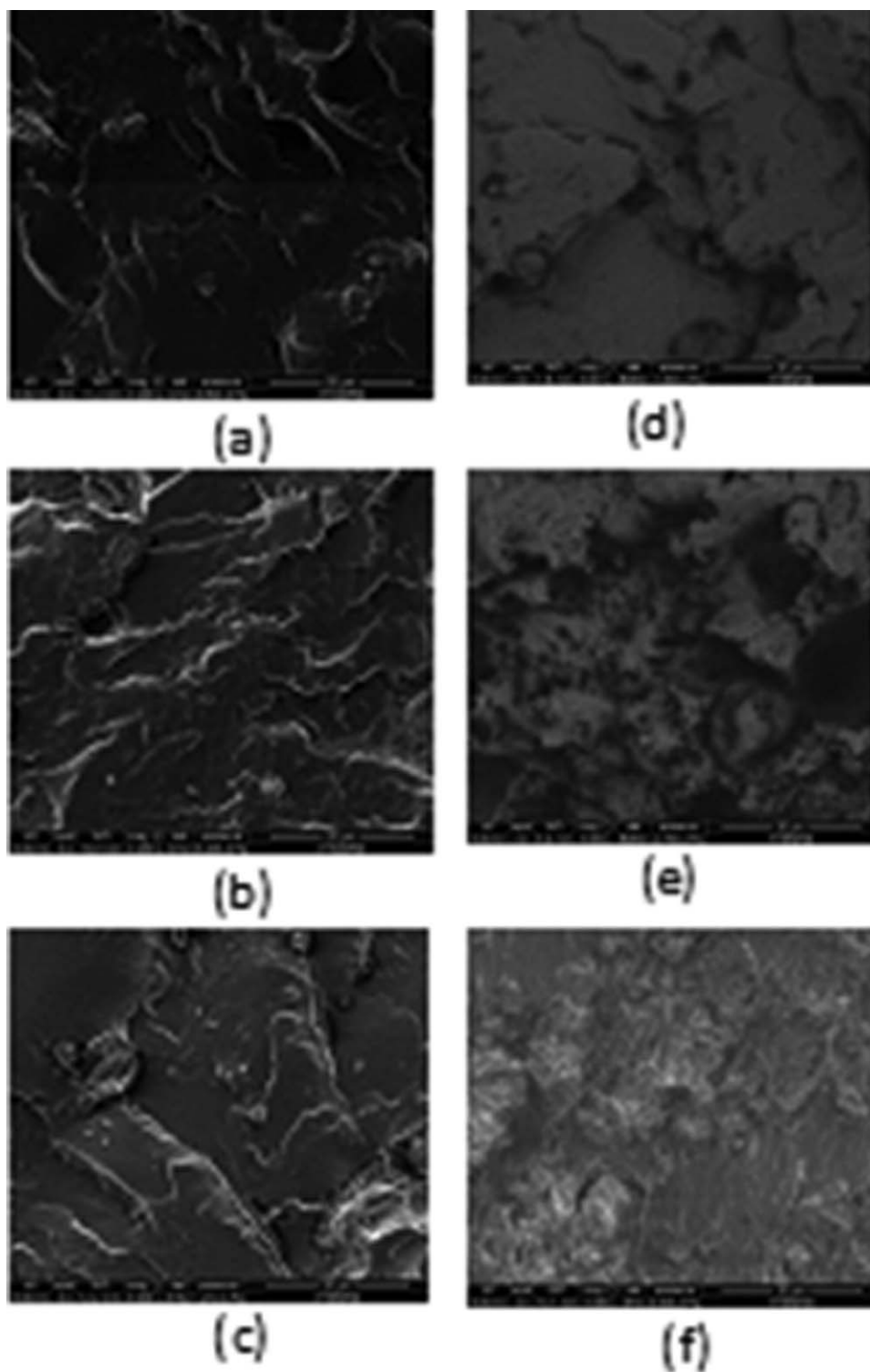
FIG. 2. SEM micrographs of fracture surfaces of the films with (a) 0% silica, (b) 2%, (c) 4%, (d) 8%, (e) 12%, and (f) 16% silica.

polymer phase was seen as a continuous matrix, indicating complete gelation of the PVC plastisol.

The properties of the films are reported in Table 1. The thickness of the films was in the range of 314–563 μm. The density of the films increased from 1.0983 to 1.2312 g/cm^3 as the silica content increased. There was 7.3% empty volume for 16% silica containing film, which could be attributed to incomplete deareation of the film owing to a high viscosity of the plastisol. The morphology of the cross-sections of the films seen in Fig. 2 also indicated the presence of empty volume. The films were elastic with an elastic modulus of 1.0–1.5 GPa. Their

SiO$_2$, %	0.0	2	4	8	12	16
Thickness, μm	524	352	314	353	563	413
Density, g/cm^3	1.0983	1.0975	1.1323	1.1575	1.2026	1.2312
Elastic modulus, GPa	1.1	1.1	1.1	1.1	1.0	1.5
Tensile strength, MPa	8.9	7.9	8.1	6.7	5.5	4.9
Elongation at break, %	81	71	75	61	55	32
Sorbed water, %	1.9	3.4	5.1	6.8	5.7	6.1
Diffusion coefficient of liquid water in composites $\times 10^{14}$ m^2/s, from Ref. [24]	3.8	3.9	3.1	4.2	6.5	9.0

tensile strengths decreased from 8.9 to 4.9 MPa and their elongation at break decreased from 81% to 32% as their silica content increased. The films sorbed 1.9 to 6.1% water in water as their silica content increased [24]. The diffusivity of the liquid water in the films increased with filler content from 3.8×10^{-14} to 9.0×10^{-14} as the silica content increased [24]. The diffusion of water occurred through empty spaces in the composites prepared by heating the plastisols. The interface between the silica and the plastic was thought to be the main path for water diffusion. The tortuous path created by the filler could have decreased the diffusivity but it was insignificant compared with the effect of empty volume and diffusion through the interface.
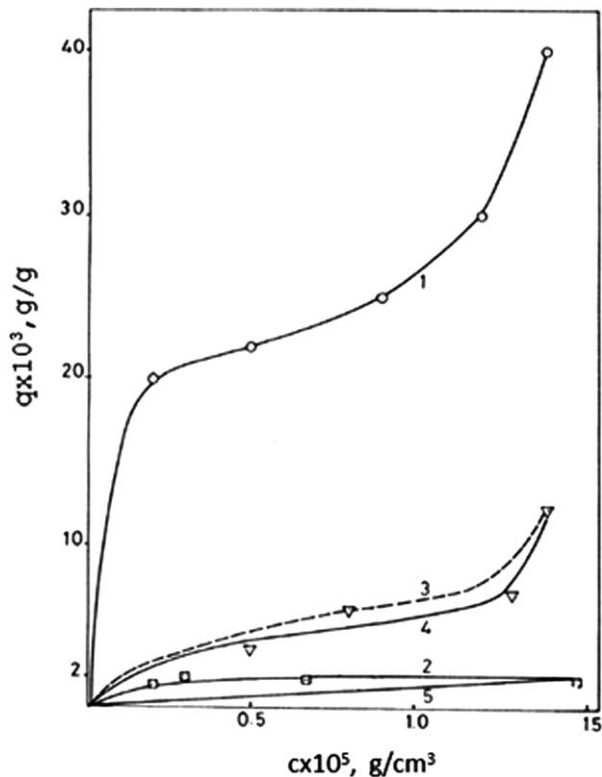

FIG. 3. Adsorption isotherms of MB on (1) silica, (2) PVC composites having 16% silica, experimental, (3) PVC composites having 16% silica, theoretical, (4) PVC powder, from Ref. [16], (5) PVC/DOP, from Ref. [16].

MB Adsorption Equilibrium Studies

Adding MB to PVC solution and film formation after evaporating the solvent [20] or adsorption of MB to swollen PVC [21] were other methods used in previous investigations. MB was introduced in the films in one step by immersing them into an aqueous solution of MB in the present study. The silica phase of the composite adsorbed MB preferentially.

Study of Adsorption on Solution Side

Adsorption capacity for MB is great for silica, and moderate for the 16% silica composite of PVC (Curves 1 and 2, respectively, in Fig. 3) as experimentally measured. Whether the additivity rule is valid for the composites is of importance to predicting their adsorption capacities. Marshall [25] showed that the adsorption capacity of PVC plastisol was additive for the adsorptivities of its components. Although that work was performed for water vapor adsorption, such an approach may also be useful for the case of MB adsorption. Therefore, Eq. 1 was used for the adsorption capacity ($q_{composite}$) prediction of the present composites, on the theoretical basis:

$$q_{composite} = \sum_{1}^{n} q_i \times m_i \qquad (1)$$

where q_i is the amount of mass adsorbed on unit mass and m_i is the mass fraction of each component in the composite structure.

MB adsorption isotherms (Fig. 3) of silica (Curve 1) and experimental and predicted MB isotherms for 16% silica composite (Curves 2 and 3) are shown together with the isotherm for PVC powder (Curve 4) and PVC/DOP plastigel (Curve 5) reported in our previous work [16]. Silica had the highest adsorption capacity of all the components. Thus, the adsorption capacity of the composite can easily be calculated by using the adsorption capacities and mass fractions of PVC and silica in the composite formulation. Such a study was carried out to construct the theoretical isotherm of composite (Curve 3 in Fig. 3). The predicted adsorption isotherm was somewhat higher and considerably higher than the experimental isotherms for PVC powder and for the (PVC-DOP)-
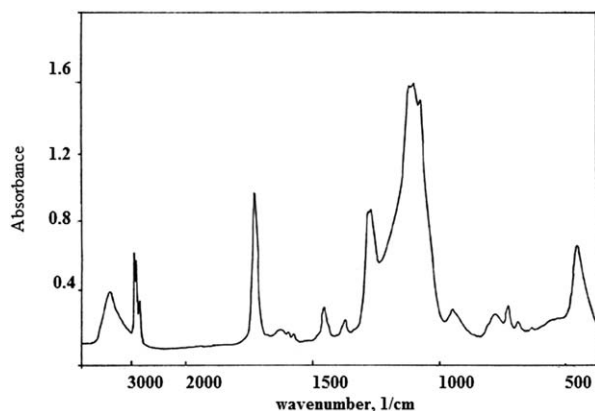
FIG. 4. IR spectrum of dried silica after the treatment with DOP/water emulsion.

silica composite, respectively. Comparison of the experimental and the predicted isotherms for the 16% silica-containing composite (Curves 2 and 3 in Fig. 3) with the isotherm of PVC/DOP composite (Curve 5 in Fig. 3) shows that the improvement in adsorption capacity of the composite by silica filler was considerable, even if it was not as high as the amount calculated by using *Eq.* 1. Since the stearates did not adsorb MB and they existed in small quantities in composites, this is mainly because of interactions between silica, which has a high oil adsorption capacity (92 cm^3 g^{-1}) [13] and DOP. Therefore, occlusion of the pores of silica by DOP to a great extent is expected. The intrusion of DOP, having a molecular diameter of 1.08 nm [22], is likely to be present in the pores of silica having BJH adsorption pore diameter of 6.83 nm. The IR spectrum of the dried silica, which was treated with water and DOP (Fig. 4), has peaks at 2,910 cm^{-1} for C—H stretching vibrations, at 1,720 cm^{-1} for C=O stretching vibrations of DOP, and 1,100 cm^{-1} Si—O stretching of vibrations of silica. From the masses of the wet and the dried sample, it was found that silica
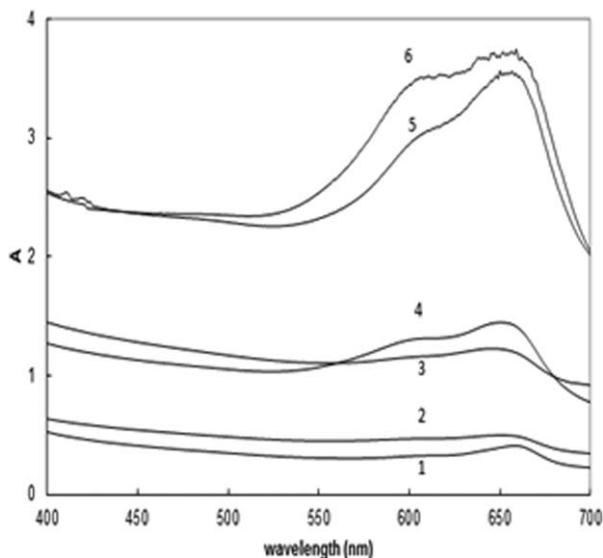

FIG. 5. Visible spectra after MB adsorption process for composites with (1) 0%, (2) 2%, (3) 4%, (4) 8%, (5) 12%, (6) 16% silica.
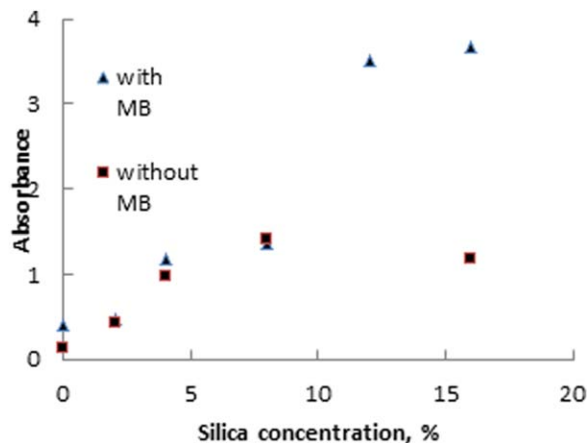

FIG. 6. Absorbance of the films at 661 nm, with respect to the amount of silica. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

absorbed 56% water and 16% DOP on a dry basis, from the DOP/water emulsion. Even if silica showed higher affinity to water than to DOP, the presence of DOP on the surface of silica in the composite was likely to prevent the adsorption of water-soluble MB. On the other hand, PVC and DOP are mutually soluble substances and the presence of DOP may inhibit the adsorption of MB by PVC in the composite.

Study of Adsorption on Solid Side and Evaluation of Optical Properties

Translucency of composite films allows them to be investigated by visible spectroscopy. The higher the amount of silica, the higher the absorbance, *A*, is of the films in the visible region, owing to the development of opacity due to silica. Small differences in sample thickness also affect the values of *A*, because they are directly proportional to sample thickness, according to the Beer-Lambert's Law. All MB dyed samples show a peak maximum at 661 nm (Fig. 5), which belongs to monomeric MB molecules [26]. There is a second peak at 610 nm, which belongs to dimers of MB. The relative intensity of the 610-nm peak compared with that of the 661-nm peak increased directly proportionally to the silica content, which indicated that as the silica content increased, the fraction of dimers of MB molecules adsorbed to the film increased. The linear increase of absorbance at 661 nm with respect to the amount of silica was also observed (Fig. 6), revealing that as the silica content increased, the amount of adsorbed MB increased.

The absorbance of films without MB at 661 nm also changed linearly with silica content (Fig. 6). The linear relation having 0.92 regression coefficient between *A* at 661 nm and silica percentage (*c*) in the films with MB can be represented by *Eq.* 2

$$A = 0.17 + 0.22c \qquad (2)$$

Optical microphotographs (Fig. 7) of MB dyed composites also confirmed that the higher the amount of silica
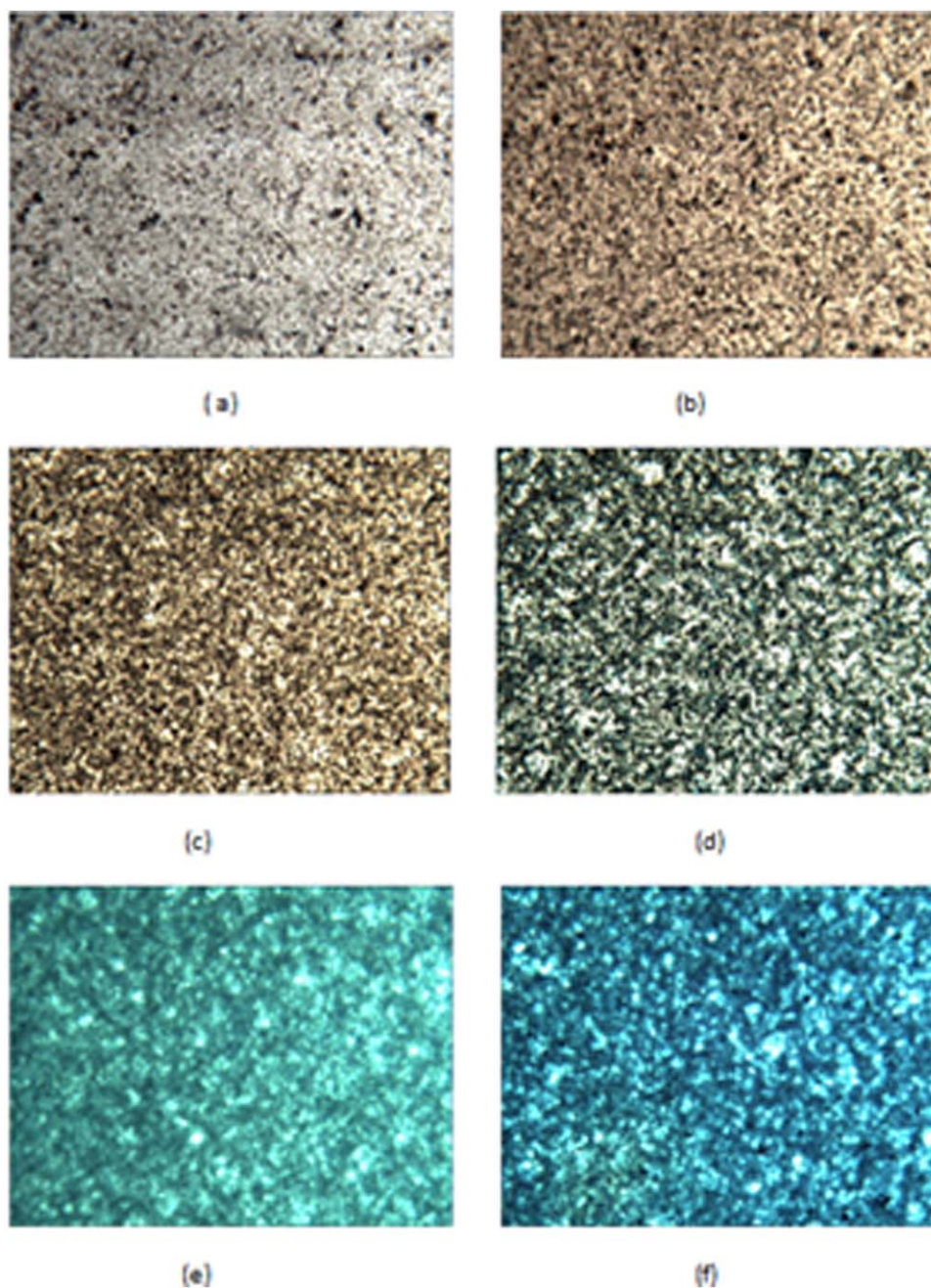
FIG. 7. Optical microphotographs of MB adsorbed composites having (a) 0%, (b) 2%, (c) 4%, (d) 8%, (e) 12%, (f) 16% silica. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is, the higher the intensity of the blue color. As it is understood from the isotherms (Fig. 3), the main adsorptive component in the composites is the silica fraction. Meanwhile, a good distribution of silica within the plastic matrix was justified by means of the microphotographs.

Kinetic Studies

When the composites were immersed in aqueous MB solution, competitive transport of mobile species, water, MB, and DOP occurred. Although water and MB diffused toward the interior of the composites, DOP diffused from the composites into the aqueous phase. It was shown that the water uptake to the composites was dependent on the silica content and it reached to a level of 6.8% for silica loading of 8% [24]. DOP migrated to the water phase until its concentration reached 0.005% [23, 24]. Compared with water transport into films, DOP transport from the films was negligible.

As the MB adsorption process progressed, MB concentration in the solution phase diminished. However, MB concentration change in the aqueous phase did not show a regular trend. Although silica has a high affinity for DOP, MB, and water, PVC is soluble in DOP and is capable of
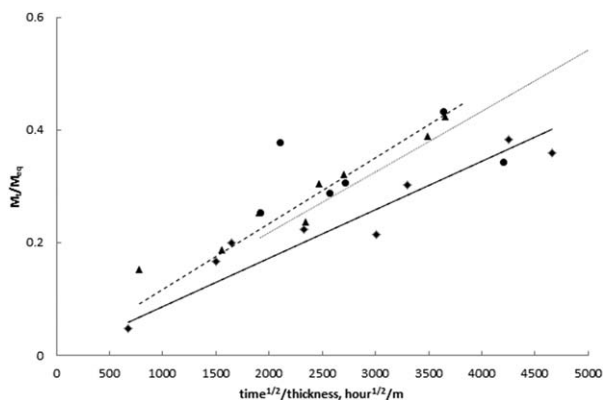
FIG. 8. Fractional uptake as M_t/M_{eq} versus the square root of time for the solid liquid ratio of 0.003 g/g. Experimental points: spheres, triangles, diamonds, and trend lines: 1, 2, and 3 for 0, 2, and 16% silica, respectively.

adsorbing MB. Adsorbed species on silica might change from DOP to water and to MB in a fluctuating and complex manner during the adsorption, owing to competitive processes. Diffusivity, so-called "apparent" instead of "true," can be obtained by carrying out the procedure of classical methods as if the process was Fickian. *Equation* 3 is used for the evaluation of short-time data of adsorption to find out the effective diffusion coefficient

$$M_t/M_{eq} = [4/l][D_e t/\pi]^{0.5} \qquad (3)$$

where M_t and M_{eq} are the adsorbed amount at time t and at equilibrium, respectively, l is half of the film thickness, and, D_e is the effective diffusion coefficient. Initial stages of (M_t/M_{eq}) versus the square root of time/thickness curves shown in Fig. 8 were evaluated. Effective diffusivities were found to be 5×10^{-13}, 6×10^{-13}, and 3×10^{-13} m^2 s^{-1} with regression coefficients of 0.73, 0.86, and 0.88 for 0%, 2%, and 16% silica-containing composites, respectively. The effective diffusion coefficient of MB in PVC-zeolite composites was also on the order of 10^{-13} m^2 s^{-1} and decreased with increasing filler fraction [16]. However, the diffusion coefficient of water in PVC-silica composites showed an increasing trend with silica content, as reported in Table 1 [24].

The diffusion mechanism of MB in plastigel films was complicated because of competitive adsorption of MB, DOP, and water on PVC and silica filler. MB is not soluble in DOP nor in PVC. It was adsorbed on the external surface of the PVC particles, having 16 m^2/g surface area dispersed in water [22]. However, PVC particles swollen with DOP were fused to each other in plastigels and the external surface area decreased to 0.044 m^2/g. Thus, a very low amount of MB was adsorbed to control the plastigel without any silica, as seen in Figs. 5 and 7.

The low gelation temperature chosen for their thermal instability of PVC was not sufficient for the complete dissolution of PVC particles in DOP and their fusion. Indeed, the DSC curves of the plastigels in Fig. 1 confirm the presence of a small amount of unplasticized PVC, because a

small shoulder belonging to a glass transition point around 80°C was obvious.

Thus, there could be interparticle spaces between the fused PVC particles swollen with DOP. The SEM micrographs seen in Fig. 2 showed the presence of pores in silica-filled composites. Mass transfer from the empty spaces between silica filler and plastic matrix could be faster than the diffusion of the MB in plasticized PVC. On the other hand, MB was preferentially adsorbed on silica particles in composites as seen in the optical micrographs in Fig. 7. However, water and DOP were also competing with MB for adsorption on silica particles. For these reasons, scattered data with a low correlation coefficient for Fickian diffusion were obtained. Although the diffusion coefficients MB for 0 and 2% silica were very close to each other, it was much lower for 16% of silica, owing to the tortuous path they should follow. The small value of the diffusion coefficient of MB in composites makes the removal of MB from aqueous solutions kinetically unsuitable. Nevertheless, it is possible to tailor a material that could be used in laser printing [20] or in making an antimicrobial medical device [21] by adsorbing MB from aqueous solutions to silica-loaded plasticized PVC.

CONCLUSION

Plastisol-plastigel technology provides a simple and inexpensive method to produce the flexible PVC-silica composite sheets. The films were elastic and their tensile strength decreased as their silica content increased. The films sorbed 1.9 to 6.1% of water from liquid water proportional to their silica content. Although the silica component provided the higher adsorption capacity, PVC matrix kept the silica particles coherent and avoided the contamination of the solution to be cleaned with dispersed silica. The diffusion coefficient of MB through the composites was 5×10^{-13}, 6×10^{-13}, and 3×10^{-13} m^2 s^{-1} for 0, 2, and 16% silica-containing composites, respectively. Because of the slow diffusion of MB in PVC-silica composites, using them as a dynamic column adsorbent was not practical. Because the silica component is the main adsorbing site, the more silica that was added to the composite, the higher the adsorption capacity was. These versatile plastics can be used wherever the dyeability is a merit, such as plastic labels, colored clothing, and leather substitutes. The MB dyed materials can be used as antimicrobial medical devices and can be printed by laser light.

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