ELSEVIER

Polymer 41 (2000) 7641–7645

polymer

Depth profiling of small molecules in dry latex films by confocal Raman spectroscopy

F. Belaroui[a], Y. Grohens[a], H. Boyer[b], Y. Holl[a,*]

[a]*Institut de Chimie des Surfaces et Interfaces, CNRS, 15, rue J. Starcky, BP 2488, 68 057 Mulhouse, France*
[b]*Jobin Yvon, 16-18 rue due Canal, 91165 Longjumeau, France*

Received 15 December 1999; received in revised form 1 February 2000; accepted 11 February 2000

Abstract

The distribution of small molecules in dry latex films is the result of driving forces competing to displace these molecules at the interfaces or to retain them distributed inside the film. In order to provide a better insight into the process leading to segregation of surfactant molecules, confocal Raman spectroscopy was used. This technique was powerful in the quantitative determination of the distribution profiles of small molecules, namely sodium dodecyl sulfate (SDS) and sulfate anion (SO_4^{2-}), active in Raman mode, in the overall thickness of polymeric films. The concentration of the SO_4^{2-} ion is higher at the film/substrate interface than in the bulk whereas the film/air interface exhibits a depletion, which propagates at 50 μm from the surface in the film thickness. An enrichment of SDS is found at both interfaces; and aggregates of small molecules inside the film were detected for both SO_4^{2-} and SDS. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Confocal Raman spectroscopy; Latex films; Butyl acrylate

1. Introduction

The growing importance of synthetic latex in domains such as adhesives, paints or non-weaved textiles is owing to their film formation and adhesion properties, and also because of ecological and economical considerations.

Film formation corresponds, when water evaporates, to a change in the system from independent particles dispersed in water to a continuous film. Three steps can be distinguished during the process of film formation [1–3]: (1) concentration of the latex; (2) deformation of the particles; and (3) diffusion of the macromolecules across the particle boundaries. During these processes the migration of surfactant molecules through the film towards the interfaces is controlled by water fluxes [4], coalescence [5], miscibility with the polymeric matrix [6–14] and ability of the surfactant molecules to lower the interfacial tension at the film/air or film/substrate interfaces [6,12]. However, during the segregation process a part of the surfactant molecules is trapped in the polymeric film and does not reach the interfaces.

Properties of the latex films such as adhesion, mechanical strength and permeability are strongly influenced by the distribution of the surfactant in the film. This explains the numerous works, which have been devoted to the fate of surfactant molecules in latex films [5,6,10–12,15–19]. Attenuated total reflection (ATR) [5,6,10–12,15] and step scan photoacoustic spectroscopy (PAS) [20] have been extensively used, but have shown some limitations in the depth probed and the quantitative interpretations, respectively.

Confocal Raman spectroscopy has shown its efficiency for depth profiling of laminates, coatings, membranes and composites [21–25]. In this paper, confocal Raman spectroscopy is shown to be a powerful quantitative technique for the depth profiling of small molecules in the overall thickness of dry latex films. The distribution profiles of sodium dodecyl sulfate (SDS) and of sulfate ion (SO_4^{2-}) in the films are investigated.

2. Experimental

2.1. Materials

Butyl acrylate (BuA) was copolymerised with 1 or 4 wt% of acrylic acid (AA) by radical emulsion polymerisation with 2.5% of surfactant (SDS). The mean particle diameter was around 100 nm, with a narrow particle size distribution. The solids content was adjusted at 25% by weight. The latex was systematically purified by dialysis at pH 10 to eliminate the surfactant used in the synthesis. Defined amounts of SDS and Na_2SO_4 were then introduced in the purified

---

* Corresponding author.

PII: S0032-3861(00)00145-2

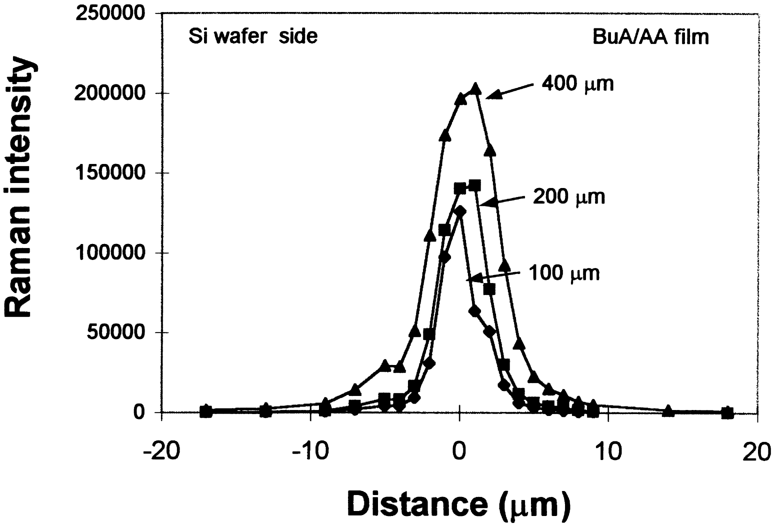

Fig. 1. Intensity of the Raman Si peak at 522 cm^{-1} for a BuA/AA 4% film on silicon as a function of the distance from the interface for different pinhole diameters: 100 μm (◆), 200 μm (■), 400 μm (▲). The negative values on the *X*-axis represent the depth in the silicon wafer and the positive values represent the depth in the polymer film.

latex. The dispersions were cast on a polyethylene substrate (parafilm) and allowed to dry under controlled conditions of temperature and relative humidity, namely, 23°C and 50%.

2.2. Technique

Raman measurements were performed with a Jobin Yvon, Labram confocal Raman spectrometer. This set up benefits from the latest advances in Raman instrumentation: a CCD camera as a detector associated with a confocal microscope and a holographic notch filter. Excitation at a wavelength of 632.8 nm was provided by an He–Ne laser. The power delivered to the sample was about 10 mW. Depth profiling was possible by tuning the plane of focus of the microscope stepwise system. Varying the diameter of the confocal pinhole from 100 to 1000 μm changes the depth resolution, which has to be estimated for each material under investigation. Fluorescence, generally due to small amounts of impurities, was never detected in the Raman signal recorded from our samples. No distortion of the spectra was observed whatever the plane of focus; the ratio of the absorbencies of two peaks belonging to the polymer remained constant at all probed depths.

The depth resolution of the confocal Raman arrangement was estimated for a pure BuA/AA 4% latex film with a thickness of 100 μm, cast on a silicon wafer. The intensity of the strong Si peak at 522 cm^{-1} was recorded as a function of the position of the plane of focus away from the film/substrate interface, for different pinhole diameters (Fig. 1). The depth resolution was determined from the full width at half maximum. It was 2.6, 3.7 and 5 μm for pinhole diameters of 100, 200 and 400 μm, respectively. No focusing was possible with a diameter of the pinhole of 1000 μm and the spectra recorded in that case were equivalent to the transmission spectra because the overall thickness of the film was probed.

Confocal Raman spectroscopy can be used for quantitative analysis since the Raman signal is known to be proportional to the concentration. BuA/AA 4% films were prepared with a concentration of SDS ranging from 2 to 30% by weight. Confocal Raman spectra of these films were recorded with an aperture of the confocal pinhole of 1000 μm. Fig. 2 shows that the ratio of the absorbencies of the SDS to the polymer peaks plotted as a function of the ratio of the concentrations is a straight line. The ratio of the molar absorption coefficients of SDS to polymer was calculated from this calibration curve as $\epsilon_{SDS}/\epsilon_{pol} = 0.648$. This value will be used for the calculation of the concentration of small molecules in the dry latex films from the confocal Raman spectra.

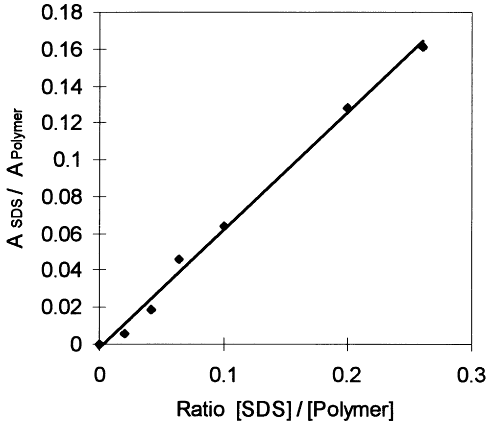

Fig. 2. Raman calibration curve for SDS in BuA/AA 4% latex films. The concentrations of SDS in the films were 2, 4, 6, 10, 20, 30%. The pinhole diameter was 1000 μm, the recorded signal thus concerned the overall thickness of the films.

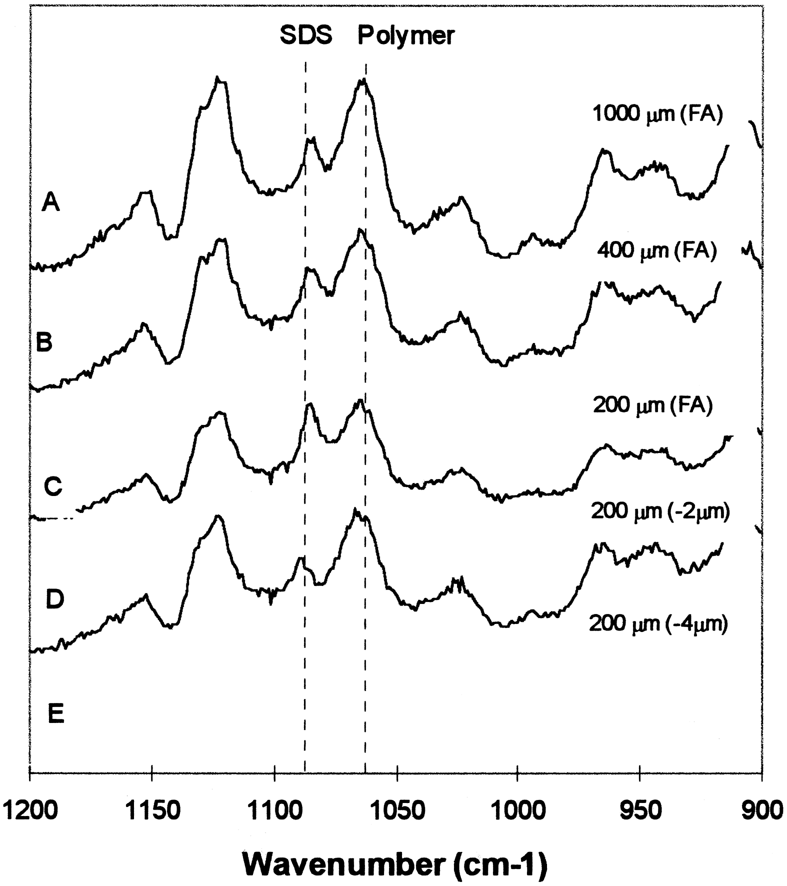

Fig. 3. Confocal Raman spectra of BuA/AA 1% latex film containing 6% of SDS. Film thickness: 85 μm. The peaks at 1084 and 1063 cm^{-1} assigned to the SDS and the polymer, respectively, are pointed in the figure. Spectra A, B and C are recorded with a plane of focus localised at the film/air (FA) interface and a pinhole diameter of 1000, 400 and 200 μm, respectively. Spectra D and E correspond to a plane of focus located at 2 and 4 μm below the FA interface, inside the film, respectively, and a pinhole diameter of 200 μm.

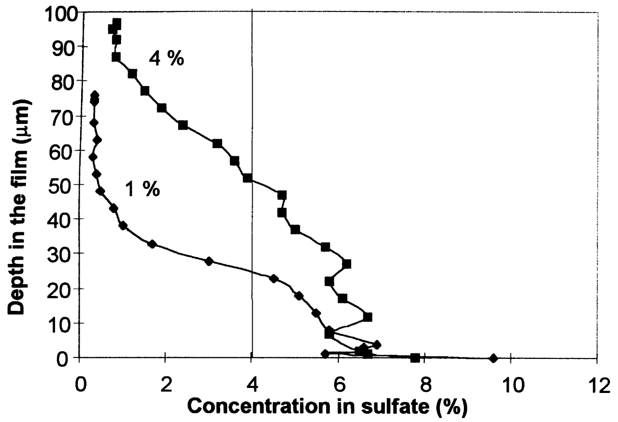

Fig. 4. Distribution profiles of the sulfate ion in the depth of the BuA/AA 1% (◆) and BuA/AA 4% (■) latex films. Pinhole diameter: 200 μm. 0 μm on the *Y*-axis corresponds to the film/substrate interface and the range of 80 to 100 μm to the film/air interface. The vertical line corresponds to the nominal concentration of SO_4^{2-} (4 wt%).

3. Results and discussion

Fig. 3 shows the Raman spectra recorded from a BuA/AA 1% film containing 6% of SDS. The peaks at 1084 and 1063 cm^{-1} are assigned to the SDS $v_{(S=O)}$ and the polymer $v_{(C–C)}$ vibrations, respectively. The plane of focus was positioned at the film/air interface and the diameter of the confocal pinhole was tuned at 1000, 400, 200 μm. Decreasing the pinhole reduces the analysed volume. The relative intensity of the SDS peak at 1084 cm^{-1} increases comparatively to the polymer peak with the decrease of the analysed volume. This is the first evidence, as will be discussed later, of the segregation of the SDS molecules at the film/air interface.

The three spectra shown at the bottom of Fig. 3 were recorded with a pinhole diameter fixed at 200 μm and a plane of focus located at the film/air interface (trace C), 2 μm (trace D) and 4 μm (trace E) below the surface, inside the film. It can be noticed that the intensity of the SDS peak at 1084 cm^{-1} decreases from the surface to 2 or 4 μm below. This first qualitative depth profiling of the SDS distribution in the film shows that the concentration of this molecule decreases rapidly inside the film, away from the surface.

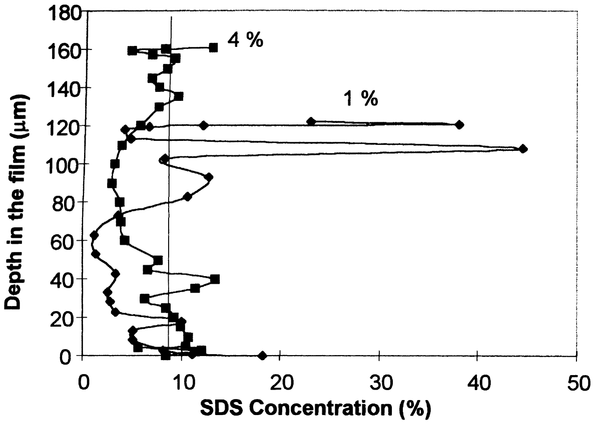

Fig. 5. Distribution profiles of SDS in the depth of the BuA/AA 1% (◆) and BuA/AA 4% (■) latex films. Pinhole diameter: 200 µm. 0 µm on the *Y*-axis corresponds to the film/substrate interface and the range of 120 to 160 µm to the film/air interface. The vertical line corresponds to the nominal concentration of SDS (6 wt%).

The concentration profiles of the sulfate ion in latex films of BuA/AA containing 1 or 4% of AA are shown in Fig. 4. The pinhole diameter was kept at 200 µm and the plane of focus was shifted by steps of 2 µm in the vicinity of the film/substrate interface (origin of the *Y*-axis), and in the vicinity of the film/air interface (top of the *Y*-axis). Inside the film, measurements were made by steps of 5 µm with a pinhole diameter of 400 µm. The vertical line drawn on the graph indicates the concentration of sulfate ion initially introduced in the latex (4 wt%). It turns out that both latex films exhibit a strong enrichment in sulfate near the film/substrate interface and a depletion at the film/air interface. This distribution can be explained by the drying process. Drying begins at the film/air interface forming a dry top layer whose thickness increases progressively. The receding drying front carries the highly water-soluble sulfate ion to the film/substrate interface, depressing its concentration near the film/air interface.

An effect of the AA content in the BuA/AA films can be observed. The difference in thickness between the two films makes a direct comparison difficult. However, one can see that the transport of SO_4^{2-} towards the film substrate interface is less efficient in the film containing more acrylic acid. This effect is likely to be due to the higher number of acidic sites in the BuA/AA 4% film, which interact with the sulfate ions and reduce their mobility.

Finally (this point is not developed in details in this short paper), in some cases, aggregates of sulfate ions are detected in the bulk of the film.

Fig. 5 shows the distribution of SDS in the BuA/AA 1 and 4% latex films. The procedure used for depth profiling was the same as for the sulfate ion. The concentration profiles recorded with SDS are markedly different from those obtained with the sulfate, mainly in the interfacial regions. Enrichment in surfactant molecules at both interfaces is observed for SDS. The main driving force for the segregation of the SDS at the interface is not the flux of water in that case, but rather the ability of the surfactant molecules to lower the interfacial tensions (film/air and film/substrate) of the latex film. Besides, the inner part of the film is depleted in SDS except for highly concentrated regions, which correspond to the localised islets of SDS. These aggregates can be crystallized, as already claimed by Kientz et al. [16]. The mechanism leading to such islets is still under investigation; however, it is assumed to be the result of a nucleation process taking place in regions of the film where the polymer/surfactant interactions are particularly strong.

It has to be noticed that the latex film containing 4% of AA exhibits a lower interfacial exudation of SDS than the film containing only 1%. This is ascribed, like in the case of SO_4^{2-}, to the polymer/surfactant interactions, which increases with the AA content, and tends to lower the ability of the surfactant to desorb from the surface of the latex particles.

Confocal Raman spectrometry has been shown to be a powerful technique for the depth profiling of molecules in latex films. It is a complementary technique for the ATR and XPS analysis as will be discussed in a forthcoming paper. It is also a promising tool for a better understanding of the fundamental mechanisms of the drying process.

Acknowledgements

We thank Rhodia for financial support. It is also a pleasure to thank Drs M. Dorget, J.F. d'Allest, C. Bonnet-Gonnet and B. Amram (Rhodia, Aubervilliers) for helpful discussions.

References

[1] Keddie JL. Mater Sci Engng R 1997;21:101–70.
[2] Winnik MA. Nomenclature. In: Lovell PA, El-Aasser MS, editors. Emulsion polymerization and emulsion polymers, New York: Wiley, 1997. p. 467–518.
[3] Winnik MA. Curr Opin Colloid Interface 1997;2:192–9.
[4] Kientz E, Holl Y. Colloids Surf, A: Physicochem Engng Aspects 1993;78:255–70.
[5] Tebelius LK, Urban MW. J Appl Polym Sci 1995;56:387–95.
[6] Zhao CL, Holl Y, Pith T, Lambla M. Br Polym J 1989;21:155–60.
[7] Vijayendran BR, Bone TL, Gajria C. J Appl Polym Sci 1981;26:1351–9.
[8] Zhao CL, Holl Y, Pith T, Lambla M. Colloid Polym Sci 1987;265:823–9.
[9] Kientz E, Holl Y. Colloid Polym Sci 1994;272:141–50.
[10] Niu BJ, Urban MW. J Appl Polym Sci 1995;56:377–85.
[11] Evanson KW, Urban MW. J Appl Polym Sci 1991;42:2287–96.
[12] Evanson KW, Urban MW. J Appl Polym Sci 1991;42:2309–20.
[13] Winnik FM, Regismond STA. Colloids Surf A: Physicochem Engng Aspects 1996;118:1–39.
[14] Tanaka T, Fujimoto T, Shibayama K. J Appl Polym Sci 1979;23:1131–6.
[15] Vanderhoff JW, Bradford EB, Carrington WK. J Polym Sci 1973;41:155–74.
[16] Kientz E, Dobler F, Holl Y. Polym Int 1994;34:125–34.

[17] Roulstone BJ, Wilkinson MC, Hearn J. Polym Int 1992;27:43–50.
[18] Tzitzinou A, Jenneson PM, Clough AS, Keddie JL, Lu JR, Zhdan P, Treacher KE, Satguru R. Prog Org Coatings 1999;35:89–99.
[19] Juhué D, Lang J. Colloids Surf A: Physicochem Engng Aspects 1994;87:177–85.
[20] Niu BJ, Urban MW. J Appl Polym Sci 1998;70:1321–48.
[21] Tabaksblat R, Meier RJ, Kip BJ. Appl Spectrosc 1992;46:60–8.
[22] Hajatdoost S, Yarwood J. Appl Spectrosc 1996;50:558–64.
[23] Hajatdoost S, Olsthoorn M, Yarwood J. Appl Spectrosc 1997;51:1784–90.
[24] Mattsson B, Ericson H, Torell LM, Sundholm F. J Polym Sci, Part A: Polym Chem 1999;37:3317–27.
[25] Schrof W, Beck E, Königer R, Reich W, Schwalm R. Prog Org Coatings 1999;35:197–204.