

Lipid Adsorption on Commercial Silica Hydrogels from Hexane and Changes in Triglyceride Complexes with Time

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ABSTRACT: The structures of and lipid complexes with two commercial silica hydrogels (Trisyl and Sorbsil 40), which contain about 60% moisture, were examined by diffuse reflectance Fourier transform infrared spectroscopy. The spectra suggested that Trisyl contained less moisture than Sorbsil 40. However, the silanol groups of Sorbsil 40 were more active in adsorbing oleic acid, triglyceride, and phosphatidylcholine (PC) from hexane than those of Trisyl. Both adsorbents strongly bound PC through the PC carbonyl and phosphate groups. Lipid adsorption from hexane solution by Trisyl depended solely on trapped moisture, while Sorbsil 40 used moisture and silanol groups on the silica surface. Spectra of triglyceride-silica hydrogel complexes, obtained 24 and 72 h after obtaining the initial spectra, showed that Sorbsil 40 adsorption was by Van der Waals forces, but the triglyceride reoriented over time with an increase in hydrogen bonding. In contrast, Trisyl initially adsorbed triglyceride by hydrogen bonding which was stable for at least 72 h. *JAOCS* 73, 693-698 (1996).

KEY WORDS: Adsorption, diffuse reflectance transform infrared spectroscopy, fatty acids, hydrogen bonding, phosphatidylcholine, triglyceride.

Adsorption bleaching is an important step in vegetable oil processing (1). Acid-activated montmorillonite clays are traditionally used to bind chlorophyll and carotenoid pigments from the oil. Phospholipid (PL) and free fatty acid (FFA) residues of previous refining steps are also bound, resulting in competition for clay adsorption sites between pigments, PL and FFA. Synthetic silica hydrogels (SH) are often added with clay to specifically bind polar species, such as PL, FFA, and soaps (2). This ensures that pigments are more effectively adsorbed by the clay without competition for adsorption sites from PL and FFA.

The structure of SH consists of approximately 60% water entrapped by a silica network. The moisture provides the polarity and hydrogen bonding capacity necessary for adsorption. While oil pigment adsorption mechanisms by clays have been proposed (3), no molecular adsorption mechanism has been reported for lipid adsorption by commercial SH. However, diffuse reflectance Fourier transform infrared spec-

troscopy (FTIR) has been used to study the mechanisms whereby silicic acid binds oleic acid (OA) (4), triglyceride (TG) (5), and PL (6) from hexane solution. These studies suggest that the OA carbonyl-oxygen, hydrogen bonds to silanol hydrogen. Furthermore, hydrogen bonding of solubilized OA to polar species in solution, i.e., isopropanol, inhibited OA adsorption (4). Adsorption of PL to silicic acid was through the phosphate group, with minimal binding through the ester bond. Adsorbent moisture promoted adsorption, probably through increased surface hydroxyls (6).

An investigation of the structure of commercial synthetic SH, lipid adsorption mechanisms, and changes in TG-SH complexes over time in a simple model system are described in this paper. More specifically, the first objective of the study was to use FTIR to examine the structure of two commercial SH, commonly used in vegetable oil processing, and compare the mode of FFA, TG, and PL adsorption from hexane solution. The second objective was to examine the change in TG bound to SH over time, by using FTIR in a simple hexane model system.

MATERIALS AND METHODS

Lipids, solvents, and adsorbents. OA and phosphatidylcholine (PC) (Sigma Chemical Co., St. Louis, MO), commercially refined TG soy oil, hexane (high-performance liquid chromatography grade), Trisyl (W.R. Grace, Columbia, MD), and Sorbsil 40 (Crosfield Group, Joliet, IL) were used.

Adsorbent structure. The structure of each SH was observed with a Mattson RS 1 FTIR instrument (Mattson Instrument Inc., Madison, WI) with diffuse reflectance unit 0030-002 (Barnes Analytical, Stamford, CT) at a resolution of 4 cm⁻¹. These conditions were used throughout unless stated otherwise (4-6). This baseline spectrum was subtracted from subsequent spectra after lipid adsorption.

OA, TG, and PC adsorption. SH (0.5 g) was added to 100 mL 0.05 M OA in hexane and stirred in a sealed vessel for 15 min (4). The adsorbent was dried under an air flow in a hood for 15 min prior to FTIR analysis. The procedure was repeated with 0.05 M TG and 0.5 mM PC solutions. A control experiment was performed by repeating the experimental procedure with 0.5 g of each adsorbent in 100 mL of hexane to

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observe moisture loss during drying. The spectral data were interpreted by examining the literature values of infrared absorption (7,8).

Change in complexed TG over time. Each SH (0.5 g) was added to 100 mL 0.05 M TG in hexane and stirred in a sealed vessel for 15 min (3–5). The adsorbent was dried under air flow in a hood for 15 min. The adsorbents were then examined by FTIR 24 and 72 h after the first spectrum was obtained. The spectrum of the unused adsorbent was subtracted from each adsorbent/lipid complex. The spectral data were interpreted by examining the literature values of infrared absorption (6,7).

RESULTS AND DISCUSSION

SH structure. Figure 1 shows the FTIR spectrum of Trisyl. The broad band between 2800–3800 cm^{-1} is the OH stretch of hydrogen-bonded water. Free silanol groups were not visible at 3747 cm^{-1} and were probably due to hydrogen bonding with water and water–water hydrogen bonding superimposed on the spectra. The bands around 1868 cm^{-1} are structural silica vibrations, while the peak at 1634 cm^{-1} are H-OH vibrations. An intense siloxane (Si-O-Si) peak is found from 1250 to 1400 cm^{-1} and silica skeletal vibrations at <1300 cm^{-1} .

Figure 2 shows the FTIR spectrum of Sorbsil 40. The peak positions were similar to those of Trisyl with peaks at 2800–3800 cm^{-1} (hydrogen bonding), 1634 cm^{-1} (hydroxyl vibrations), and 1250–1400 cm^{-1} (siloxane). In contrast, the spectrum obtained with Sorbsil 40 showed a much larger peak at 2800–3600 cm^{-1} relative to the siloxane peak (1250–1400 cm^{-1}).

Silicic acid peaks (4) were similar to those of Trisyl but differ from both SH in that the ratio of the water (2800–3750 cm^{-1}) to the siloxane peak (1250–1400 cm^{-1}) was reduced.

The adsorption data reported should not be used as a means for comparing the commercial value of the adsorbents because they were obtained from a hexane solution and the

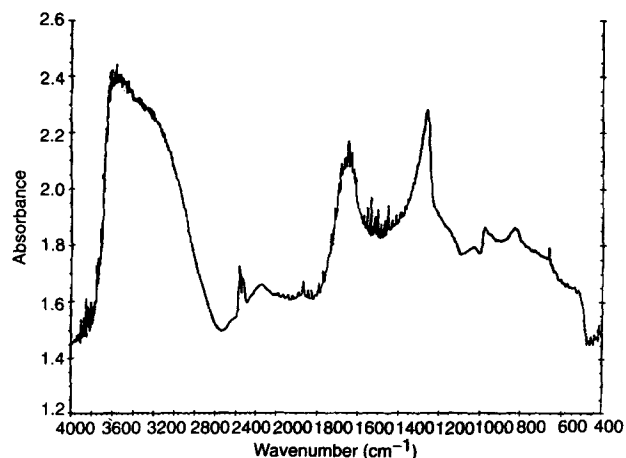


FIG. 2. Diffuse reflectance Fourier transform infrared spectrum of Sorbsil 40 (Crosfield Group, Joliet, IL).

adsorbents. This was in contrast to the industrial oil bleaching conditions under which these materials were used.

Control study. Figure 3 shows the FTIR subtraction spectrum of Trisyl after washing in hexane and drying. The spectrum shows considerable noise in the 3000 to 3800 cm^{-1} region due to the subtraction of one large water band from another. The corresponding FTIR subtraction spectrum of Sorbsil 40 in Figure 4 shows a large negative peak at 3650 cm^{-1} and suggests considerable moisture loss.

OA adsorption. Figure 5 shows the FTIR spectrum obtained after adsorption of OA to Trisyl, with subtraction of the Trisyl spectrum. The small negative silanol group at 3714 cm^{-1} indicates a small amount of hydrogen bonding to surface silanol. The hydrogen-bonded silanol stretch has shifted from that of the free form at 3747 cm^{-1} due to the surface silanol groups already engaging in some hydrogen bonding with other surface silanol groups. The peak at 1306 cm^{-1} was the remainder of the siloxane peak after subtraction.

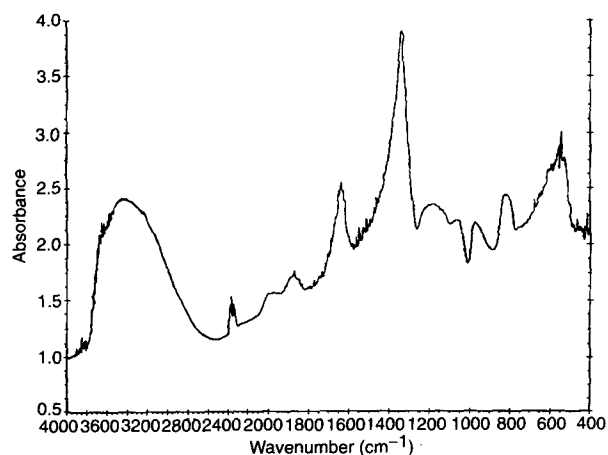


FIG. 1. Diffuse reflectance Fourier transform infrared spectrum of Trisyl (W.R. Grace, Columbia, MD).

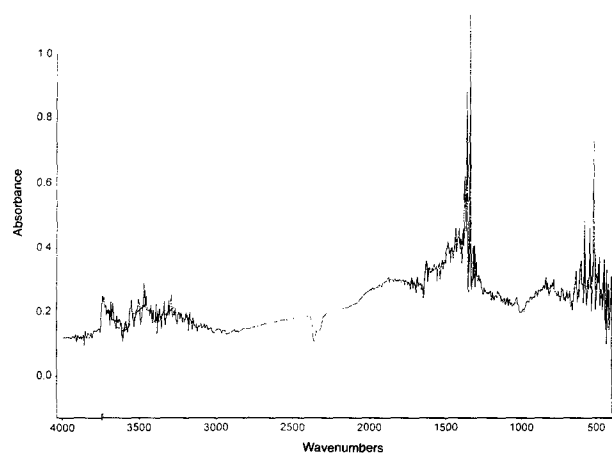


FIG. 3. Diffuse reflectance Fourier transform infrared spectrum of Trisyl after incubation with 100 mL of hexane for 15 min with the Trisyl spectrum subtracted. See Figure 1 for company source.

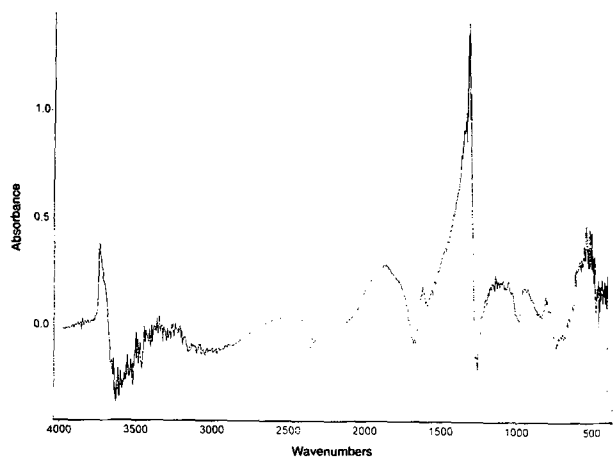


FIG. 4. Diffuse reflectance Fourier transform infrared spectrum of Sorbsil 40 after incubation with 100 mL of hexane for 15 min with the Sorbsil 40 spectrum subtracted. See Figure 2 for company source.

The carbonyl stretch of the adsorbed OA shifted to 1716 cm^{-1} relative to 1712 cm^{-1} of free OA. The small shift indicates only weak carbonyl/silanol hydrogen bonding and OA existing as dimers on the surface.

The asymmetric C-H stretch (2828 cm^{-1}) was greater than the C-H symmetric stretch (2856 cm^{-1}), indicating little or no interaction of OA hydrocarbon chains with the surface.

An FTIR spectrum of OA adsorbed on Sorbsil 40, with the adsorbent spectra subtracted, is in Figure 6. The negative silanol peak (3627 cm^{-1}) was due to moisture loss as shown by the control experiment with hexane (Fig. 4). The small negative peak at 3750 cm^{-1} indicated a small amount of OA hydrogen bonding to surface silanol groups.

The carbonyl stretch of adsorbed OA (1720 cm^{-1}) shifted from that of the free form (1712 cm^{-1}), which suggested some hydrogen bonding of OA with silanol sites and bound water.

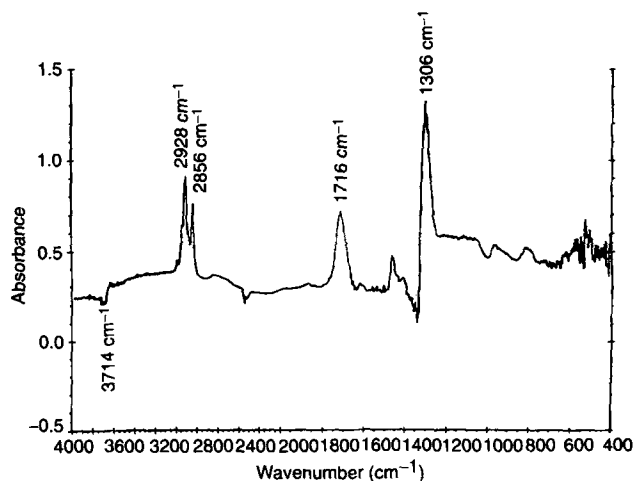


FIG. 5. Diffuse reflectance Fourier transform infrared spectrum of Trisyl after incubation with 100 mL of 0.05 M oleic acid in hexane for 15 min with the Trisyl spectrum subtracted. See Figure 1 for company source.

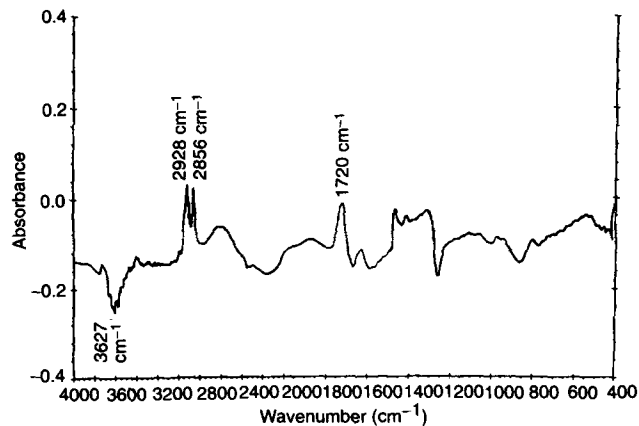


FIG. 6. Diffuse reflectance Fourier transform infrared spectrum of Sorbsil 40 after incubation with 100 mL of 0.05 M oleic acid in hexane for 15 min with the Sorbsil 40 spectrum subtracted. See Figure 2 for company source.

Carboxyl carbonyl and hydroxyl were probably hydrogen bonding to form a monomeric cyclic complex (9). However, the asymmetric C-H stretch (2928 cm^{-1}) was only slightly larger than the C-H symmetric stretch (2856 cm^{-1}), indicating some interaction of OA hydrocarbon chains with the surface because the intensity ratio changed from that of free OA.

TG adsorption. Figure 7 is an FTIR spectrum obtained when TG was adsorbed on Trisyl from hexane, with the adsorbent spectrum subtracted. The small negative silanol peak (3714 cm^{-1}) shifted, relative to free silanol groups (3747 cm^{-1}), suggesting strong silanol-silanol and silanol-water interactions. The carbonyl band maximum (1750 cm^{-1}) also shifted relative to the free TG carbonyl (1745 cm^{-1}). The continued adsorption at 1745 cm^{-1} suggested that not more than one carbonyl of the TG molecule was involved in hydrogen bonding. The fact that the C-H asymmetric stretch (2928

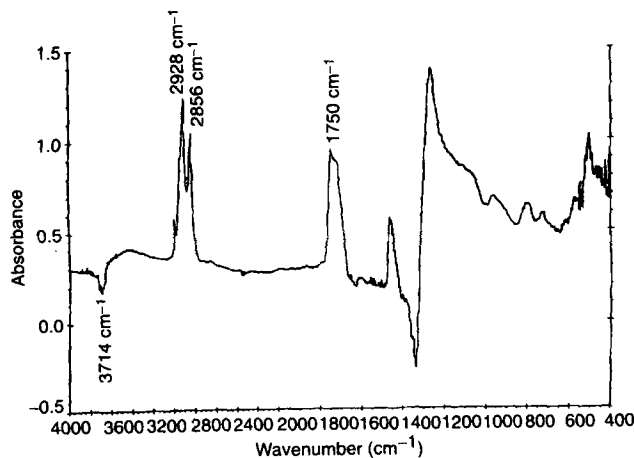


FIG. 7. Diffuse reflectance Fourier transform infrared spectrum of Trisyl after incubation with 100 mL of 0.05 M triglyceride in hexane for 15 min with the Trisyl spectrum subtracted. See Figure 1 for company source.

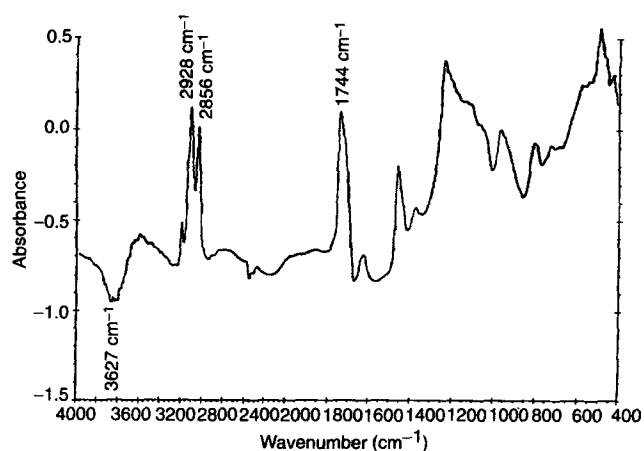


FIG. 8. Diffuse reflectance Fourier transform infrared spectrum of Sorbsil 40 after incubation with 100 mL of 0.05 M triglyceride in hexane for 15 min with the Sorbsil 40 spectrum subtracted. See Figure 2 for company source.

cm^{-1}) was greater than the C-H symmetric stretch (2856 cm^{-1}), as in free TG, indicated that the hydrocarbon chains were not interacting with the surface.

Figure 8 is an FTIR spectrum obtained when TG was adsorbed on Sorbsil 40 from hexane, with the adsorbent spectrum subtracted. The negative silanol peak (3627 cm^{-1}) was again due to moisture loss during adsorption. The carbonyl stretch (1744 cm^{-1}) shifted little relative to that of the free form (1745 cm^{-1}). This may have been due to the C-O-C of the ester bond binding to the adsorbent. The ratio of the C-H asymmetric stretch (2928 cm^{-1}) to that of the symmetric stretch (2856 cm^{-1}) indicated that the hydrocarbon chains did not interact with the surface.

PL adsorption. An FTIR spectrum obtained when PC was adsorbed on Trisyl from hexane, with the adsorbent spectrum subtracted, is given in Figure 9. The small negative silanol peak (3714 cm^{-1}) indicated only a small amount of hydrogen bonding to surface silanol groups. The carbonyl stretch (1731 cm^{-1}) shifted from the free form (1741 cm^{-1}). Therefore, the PC carbonyls were interacting with the adsorbent moisture. The lack of PC phosphate stretches indicated strong phosphate/water association (6).

Figure 10 shows the FTIR spectrum obtained on adsorbing PC onto Sorbsil 40 from hexane solution, with the adsorbent spectrum subtracted. The carbonyl group (1731 cm^{-1}) intensity and the C-H intensities (2928 cm^{-1}) and (2856 cm^{-1}) were small, suggesting that little PC was adsorbed. The negative peak at 3627 cm^{-1} was due to moisture loss in the adsorption process.

Changes in complexed TG over time: Sorbsil 40. Immediately after adsorption, the carbonyl band at 1747 cm^{-1} shifted from 1745 cm^{-1} of the nonbound TG carbonyl (Fig. 8), suggesting little carbonyl involvement in H-bonding (2). After 24 h, non-H-bonded (1745 cm^{-1}) and H-bonded (1731 cm^{-1}) carbonyl peaks were evident, with the peak at 1745 cm^{-1}

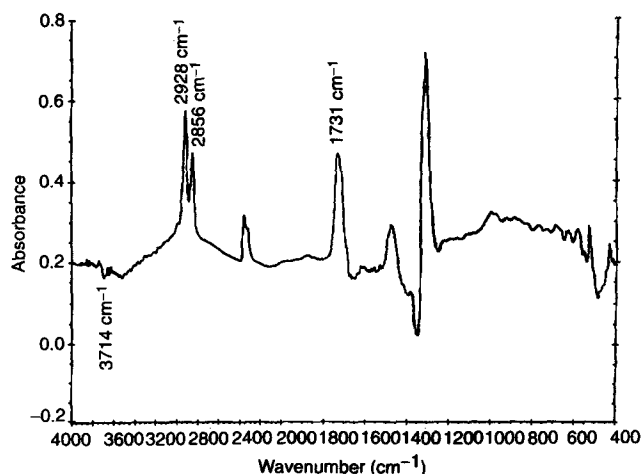


FIG. 9. Diffuse reflectance Fourier transform infrared spectrum of Trisyl after incubation with 100 mL of 0.5 mM phosphatidylcholine in hexane for 15 min with the Trisyl spectrum subtracted. See Figure 1 for company source.

being larger (Fig. 11). This may indicate an increase in the number of TG ester carbonyls being involved in H-bonding. After 72 h, the non-H-bonding carbonyl peak (1745 cm^{-1}) was smaller than that of the H-bonded peak (1729 cm^{-1}) (Fig. 3), showing increased TG carbonyl H-bonding over time (Fig. 12).

The data suggested that TG undergoes a positional rearrangement on the adsorbent over time. TG may reorient to adopt the most thermodynamically stable position to enable the maximum H-bonding of the three carbonyl groups. The changes in the negative silanol stretch indicated a rearrangement, or loss of water over time. This change of water distribution would enable the TG to adopt the most thermodynamically favorable orientation to expose the maximum number

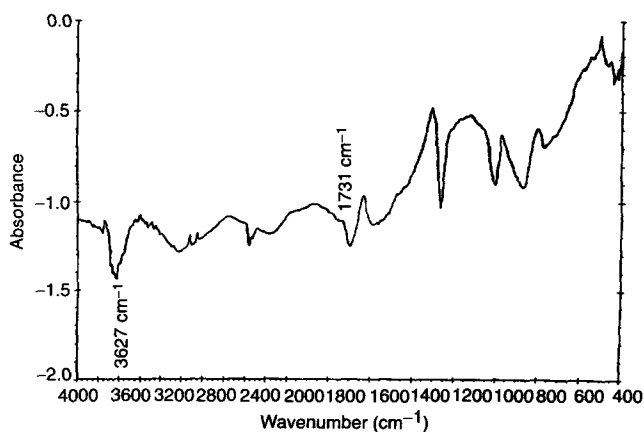


FIG. 10. Diffuse reflectance Fourier transform infrared spectrum of Sorbsil 40 after incubation with 100 mL of 0.05 M triglyceride in hexane for 15 min with the Sorbsil 40 spectrum subtracted. See Figure 2 for company source.

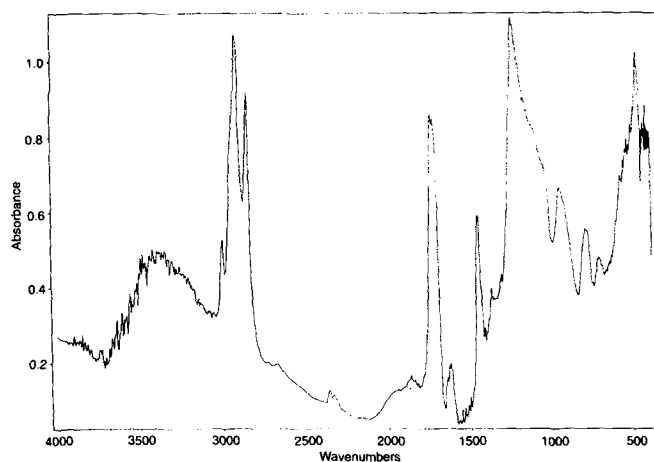


FIG. 11. Fourier transform infrared spectrum of 0.5 g Sorbsil 40 after incubation with 100 mL 0.05 M soy oil triglyceride in hexane for 15 min, dried, and stored for 24 h. See Figure 2 for company source.

of carbonyls to polar sites. However, the TG was intact without any indication of hydrolysis.

Trisyl. The shift in the 3714 cm^{-1} band, found immediately after adsorption (Fig. 7), to 3724 cm^{-1} after 24 h (Fig. 13) suggested that the TG was shifting with time to silanol sites with less silanol–silanol and silanol–water interactions. This trend continued with time, as shown by the negative peak shift to 3732 cm^{-1} after 72 h (Fig. 14).

Shifting of the pure TG carbonyl band at 1745 to 1729 cm^{-1} immediately after adsorption (Fig. 7) suggested that some of the TG carbonyl groups are H-bonded. After 24 h (Fig. 13), the carbonyl has shifted a little further to 1725 cm^{-1} , showing slightly more TG carbonyl H-bonding, which was maintained after 72 h (Fig. 14).

It required 72 h for the carbonyl peak on Sorbsil 40 to shift to 1729 cm^{-1} . This suggested that the greater amount of water in Sorbsil 40 inhibited the TG reaching suitable H-bonding sites on the surface. This was consistent with our previous

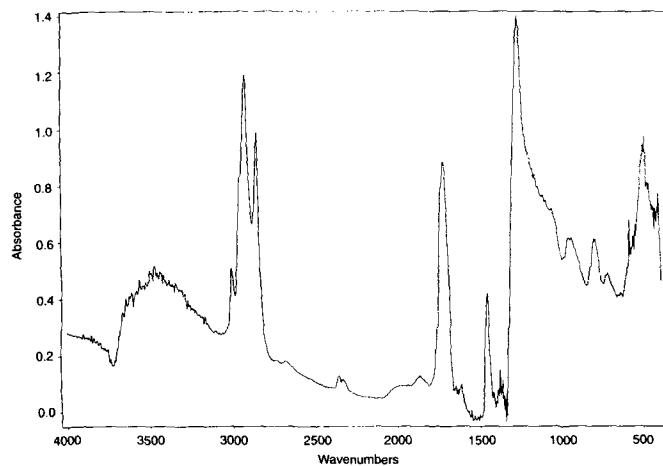


FIG. 12. Fourier transform infrared spectrum of 0.5 g Sorbsil 40 after incubation with 100 mL 0.05 M soy oil triglyceride in hexane for 15 min, dried, and stored for 72 h. See Figure 2 for company source.

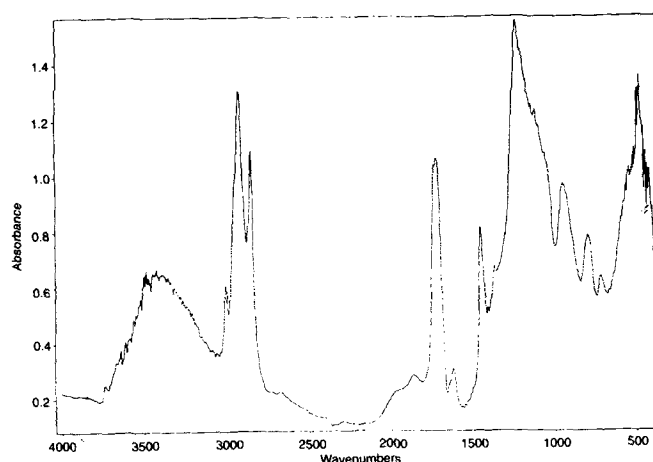


FIG. 13. Fourier transform infrared spectrum of 0.5 g Trisyl after incubation with 100 mL 0.05 M soy oil triglyceride in hexane 15 min, dried, and stored for 24 h. See Figure 1 for company source.

finding of much larger H-bonding effects for TG adsorption on silicic acid (9), which had a much lower water content than Sorbsil 40 and Trisyl.

Adsorption to both adsorbents was greater with associated moisture rather than with a silica surface. However, the FTIR data suggested that Trisyl hydrogen-bonded OA and TG to a small extent to surface silanol groups. Both adsorbents bound PC through phosphate groups, but the more diminished C-H and carbonyl stretches of Sorbsil 40 suggested little adsorption on Sorbsil 40. It should be realized that this study should not be used as a basis for comparing commercial effectiveness of the silica gels because it was an investigation of the mode of adsorption and not binding capacity. Furthermore, the experimental conditions were not those for which these commercial adsorbents were designed. Nevertheless, the data demonstrated significant differences between Trisyl and Sorbsil 40. Monitoring the TG Trisyl complex showed that hydrogen bonding was maintained over time. In contrast,

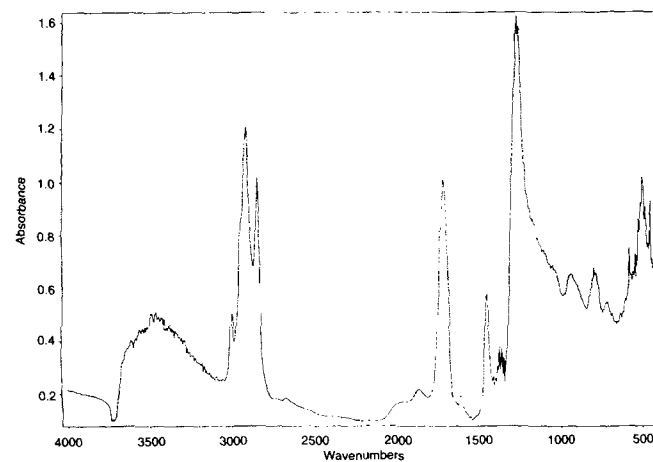


FIG. 14. Fourier transform infrared spectrum of 0.5 g Trisyl after incubation with 100 mL 0.05 M soy oil triglyceride in hexane 15 min, dried, and stored for 72 h. See Figure 1 for company source.

Sorbsil 40 probably initially adsorbed TG by Van der Waals forces, and the molecules reoriented over time to form some H-bonds with the surface. Loss of moisture from Sorbsil 40 over time may have interfered with the subtraction spectrum in the region of the silanol stretch. This was not as evident with Trisyl because of the greater moisture content of Sorbsil 40. However, there was no indication of TG hydrolysis observed on either adsorbent.

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