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Flow Micro-Calorimetry and FTIR Spectroscopy Study of Interfacial Interactions in Uncoated and Coated Calcium Carbonate Filled Polyurethane Adhesives

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Summary: Thermoplastic polyurethane (TPU) - calcium carbonate interactions were studied using flow micro-calorimetry (FMC) and diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS). FMC enabled the determination of adsorption and desorption energies; in this study a model compound approach was used to acquire insight in to the effect of calcium carbonate type and presence of stearate coating on polymer – filler interactions. It was anticipated that this data will assist in the understanding of differing responses obtained from parallel plate rheometry and viscoelastic measurements of the filled polyurethanes. Three calcium carbonates (coated and uncoated precipitated calcium carbonate, and natural ultramicronized uncoated calcium carbonate) were used. A stronger TPU-filler interaction was shown in the uncoated precipitated calcium carbonate due to the fact that more of the surface was available for interaction.

Keywords: FMC; DRIFTS; thermoplastic polyurethane; adhesive; calcium carbonate.

Introduction

The structure of the polyurethanes determines their properties and this can be altered by adding fillers due to the creation of polymer-filler interactions [1, 2]. For a given interfacial area in the composite, the overall strength of these interactions is dependent on the native surface chemistry of the filler and any surface modification that may be applied to it. In order to fully understand the properties of the filled polyurethane as adhesive, these interactions must be understood and controlled. Parallel plate rheometry and viscoelastic measurements can be used to assess the polyurethane-filler interactions but they are limited due to the absence of quantitative data concerning the polymer – filler interactions at a molecular level. In this study, flow micro-calorimetry (FMC) measurements, supported by diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) will be targeted towards quantification of these interactions.

FMC can be used to investigate the interfacial interactions between solids and liquids by determination of the heats of adsorption/desorption [3, 4]. Different fillers including carbon black, silica, and organo-clays have been examined using FMC. The latter fillers in particular are often modified using chemical treatments in order to improve the chemical and/or physical adsorption characteristics of polymer matrix chains on to their surfaces [4-9]. For example, silica is able to interact with polar adsorbates via hydrogen bonding interactions with surface silanol groups (i.e., isolated, germinal, vicinal varieties) and siloxane bridges [9]. However, some grades of carbon black and calcined silicas typically show van der Waals or hydrophobic bond interactions with polymers.

Akoum et al. [10] modified fumed silica by grafting with trimethylchlorosilane and analysed the adsorption of poly(dimethylsiloxane) elastomers on silica by using FMC. They concluded that the conformation of the macromolecules on silica depends on the silica surface area which was correlated with surface-polymer interactions. During the last five years, FMC has been used in studies of: bio-diesel fuel manufacture, waste control, organic pollutants and catalysts, within the pharmaceutical, chemical and polymer industries [11, 12]. However, the use of FMC in studies of interfacial interactions in thermoplastic polyurethane (TPU) composite adhesives has not been reported in the literature. In this study a model compound will be used to simulate the structural units of a TPU adhesive. As the segmented structure of TPUs used for adhesive applications, is mainly dominated by polyester polyol based soft segments, dimethyl adipate was selected for use as a probe molecule to simulate the interactions between polyester polyol and the various filler samples investigated.

Experimental Part

Materials

Two coated (Socal®312) and uncoated (Socal®31) precipitated calcium carbonates (PCC) supplied by Solvay Specialités (Salin de Giraud, France), and natural ultra-micronized uncoated calcium carbonate Microcarb®95 (GCC) supplied by Reverté (Barcelona, Spain) were investigated. Selected properties of these calcium carbonates are given in Table 1. The filler particle shape, size and size distribution of some of them were visually assessed using TEM (Figure 1). The PCC samples had primary particles which were on average less than 100 nm and could be accurately described as nanoparticles, GCC however, had particles closer to 1 μm in size [13], the latter were also rather random in shape.

Table 1. Selected properties of the calcium carbonates (taken from the technical data sheets) [14, 15].

Calcium carbonates	$CaCO_3$ content (wt%)	Free flowing density (g/l)	Specific surface area (m^2/g)	Mean particle size (nm)
Uncoated natural	98.96	500	13	605
Uncoated PCC	98.90	210	20	70
Coated PCC	98.90	286	19	70

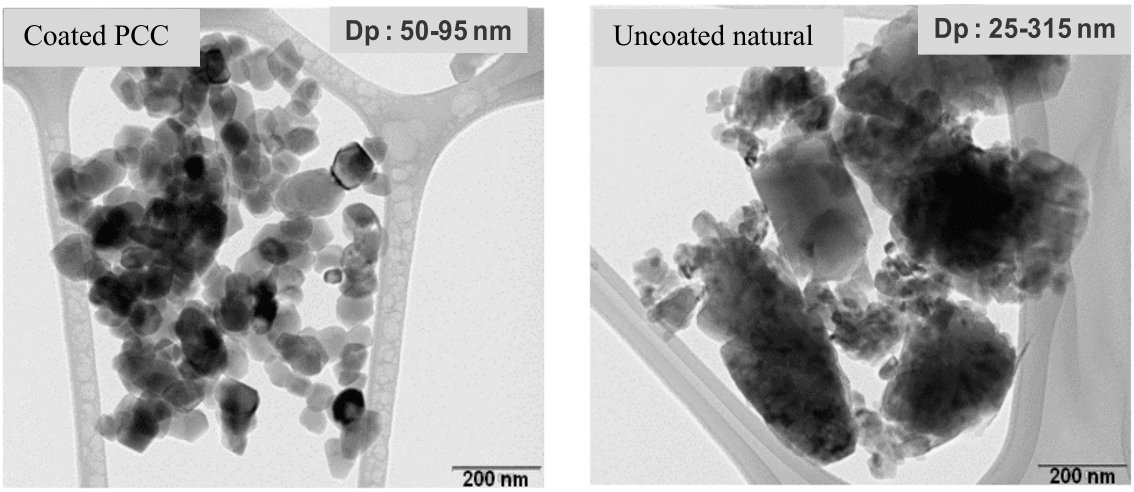

Figure 1. TEM micrographs of coated precipitated and uncoated natural calcium carbonate [13].

The coated PCC is treated to a level of 4 % wt stearate (most likely ammonium stearate). Figure 2 shows the TGA curve (together with the associated derivative (DTGA) data) of the coated PCC where the mass losses at 386 ºC and 459 ºC correspond to loss of stearate [16, 17]. It is highly probable that PCC was coated with ammonium stearate as no traces of calcium or other metals can be detected in the chemical analysis of the coated filler by X-ray fluorescence spectroscopy.

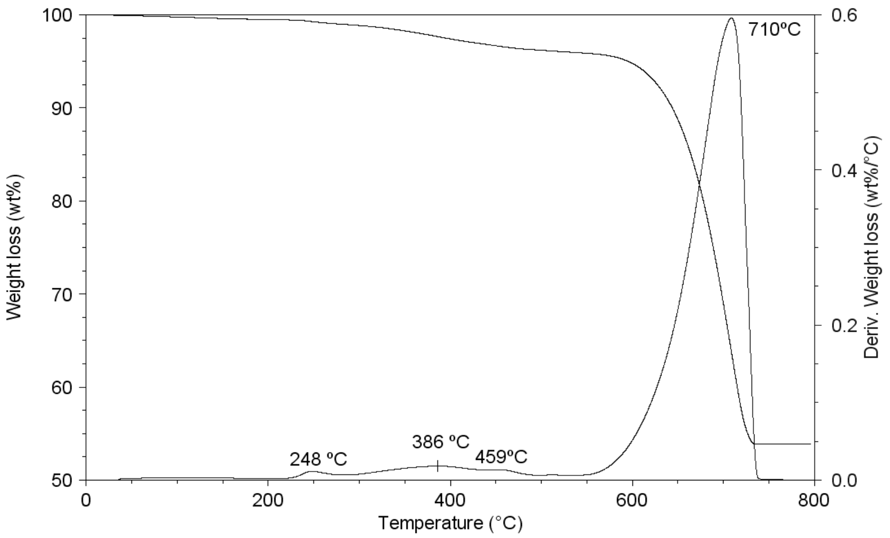

Figure 2. TGA and DTGA data obtained for the coated PCC.

Experimental Techniques

Characterization of the calcium carbonates

Transmission electron microscopy (TEM). A Jeol TEM-2010 instrument (Tokyo, Japan) was used to analyse the topography and measure the particle size of calcium carbonates; an acceleration voltage of 100 kV was used. A low concentration suspension of particles in ethanol was prepared and was treated by using an ultrasonic bath during 3-4 minutes. A drop of dispersion was put on a Lacey grid of 3.05 mm of diameter and ethanol was removed at room temperature.

Thermogravimetric analysis (TGA). The mass loss versus temperature characteristics of coated calcium carbonate was measured in a TA Instruments (New Castle, USA) Q500 TGA instrument. The samples (10 – 15 mg) were contained in platinum pans and were heated from room temperature to 800ºC at a heating rate of 10ºC/min under a nitrogen atmosphere (flow rate: 100 ml/min).

Characterization of the TPU films

Dynamic mechanical thermal analysis (DMTA). The viscoelastic properties (closely related to the strength of filler-polymer interactions) of the filled polyurethanes were measured using a TA Instruments (New Castle, USA) DMA Q800 instrument. The experiments were carried out in the shear sandwich mode (sample dimensions: 10 mm x10 mm x 1 mm), over the temperature range -100ºC to 80ºC, heating rate was 5ºC / min. Oscillation frequency and strain amplitude were 1 Hz and 0.5%, respectively.

Quantification of polyurethane-calcium carbonate interactions

Flow Micro-Calorimetry (FMC). The FMC instrument used was a Microscal 3V with PTFE cell. The cell outlet was connected to a Waters 410 differential refractometer. The data outputs were handled by Perkin-Elmer Nelson 970 series interface connected to PC. The volume of the sample chamber was 0.15 cm^3 (sufficient filler was used to fill the chamber), experiments were carried out at cell temperature of 20 °C (± 1 °C). Adsorption experiments were carried out from both heptane and butan-2-one, at a flow rate of 4.0 ml/h. The concentration of the probe solution was 0.3 % w/v. Decahydronaphthalene was used as the non-adsorbing probe.

The butan-2-one and heptane were HPLC grade and dried over 3A molecular sieves. The adsorption and desorption of dimethyl adipate (99%, Aldrich, UK), from both heptane and butan-2-one, on to the calcium carbonate samples was investigated at 20 °C according to established FMC methods [4-12]. After completion of the FMC experiments, the fillers were oven dried at 70 ºC for 20 hours, and were examined using diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS). The adsorption of the actual TPU from butan-2-one was also attempted, but unfortunately the cell blocked due to formation of a plug of what was effectively a TPU/calcium carbonate composite in the cell. Therefore an adsorption isotherm type approach (described below) had to be adopted for studying adsorption of the TPU from butan-2-one.

Solution adsorption of TPU on to the filler samples. TPU adhesive solutions (0.1-5.0 wt%) in butan-2-one were used for the adsorption study, which was carried out by stirring 9 ml of each TPU solution with calcium carbonate (0.5 g). After 12-16 hours the samples were filtered, washed with fresh heptane and dried at 70ºC for 4 hours in an oven and were analysed using DRIFTS.

Diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS). The species adsorbed on the calcium carbonates were analysed quantitatively by using a Thermo-

Nicolet Nexus spectrometer fitted with the standard DTGS detector and Spectra-Tech DRIFTS cell. Prior to analysis, the samples were diluted to 5 % wt with finely ground KBr; care was taken to gently fold the sample in to the KBr, in order to avoid damaging the filler particles. Spectra were made up of 160 scans with resolution set to 4 cm^{-1}. The spectra were normalized by using the automatic baseline correct tool and the peak area ratio (A_{1731}/A_{1794}) was determined from peak areas at 1731 cm^{-1} (ν_{st} C=O from urethane) and 1794 cm^{-1} (ν_{st} C=O from calcium carbonate) by using Omnic 5.1 software.

Results and Discussion

DMTA studies

Coated calcium carbonate may be used to control the rheology of the adhesive solution, and to improve the viscoelastic properties of the polyurethane [13]. DMTA studies revealed (Figure 3(a)) that at 5 wt % filler content, stearate coated PCC led to lower G′ than the uncoated GCC. The behaviour observed may be related to differences in filler-matrix interaction; there is higher filler-matrix interaction in the composite based on uncoated GCC due to the somewhat depressed tan delta peak (Figure 3(b)). The increased interfacial area in the coated PCC based composite was overshadowed the increased filler–matrix interaction in the composite based on untreated GCC, thereby indicating that the reduction in filler-matrix interaction arising from stearate modification is significant. FMC studies will confirm the effect of stearate treatment on filler–matrix interaction.

FMC studies of adsorption of dimethyl adipate onto the calcium carbonates

Data in Figure 4(a) shows the heats of adsorption and desorption of dimethyl adipate (DA) from heptane on to the various calcium carbonate samples, whilst data for adsorption of DA from the more polar butan-2-one on to the same substrates are shown in Figure 4(b). It is immediately apparent that the untreated calcium carbonates generally show more energetic adsorption relative to the stearate treated sample, this is consistent with other studies [18-21] that come to the same conclusion. The other obvious effect is that the heats of adsorption from butan-2-one are substantially lower due to the stronger interactions between the solvent and the substrates (Figure 4(c)). In this case the highest energy adsorption sites may be blocked by the solvent molecules. Despite the latter, the uncoated PCC sample still showed more energetic adsorption of DA. However, the uncoated GCC showed much less energetic adsorption of DA than the uncoated PCC, an effect that may be related to the interaction of natural organic matter on the surface of the GCC with the butan-2-one. The heats of desorption of DA from heptane (Figure 4(a)) are greater than the heats of adsorption of DA. This is most likely to be an artefact of the peak integration process, though it may be also associated with water being desorbed together with the DA. Desorption of filtration aids cannot be ruled out either. The DRIFTS data (see below) clearly shows retention of DA on the filler surfaces.

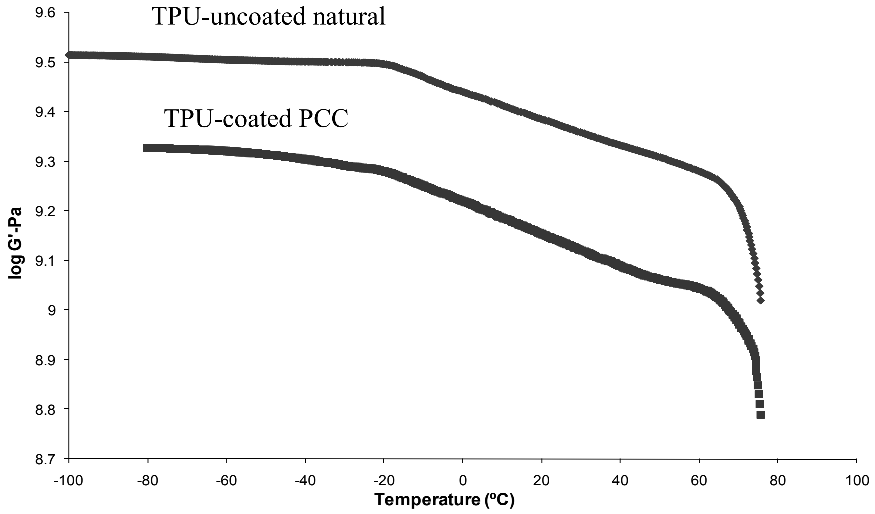

Figure 3a. DMTA data showing storage modulus (G′) as a function of the temperature for TPU composites containing 5 wt% of the indicated calcium carbonate samples.

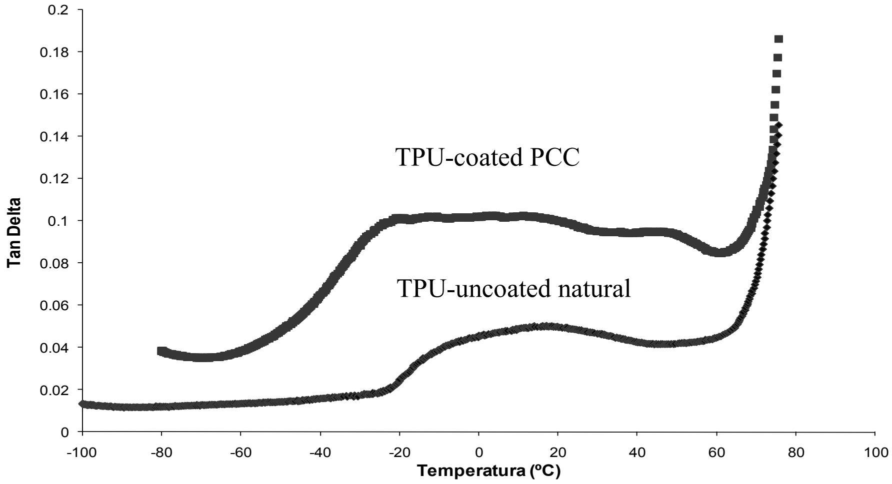

Figure 3b. DMTA data showing Tan delta as a function of the temperature for TPU composites containing 5 wt% of the indicated calcium carbonate samples.

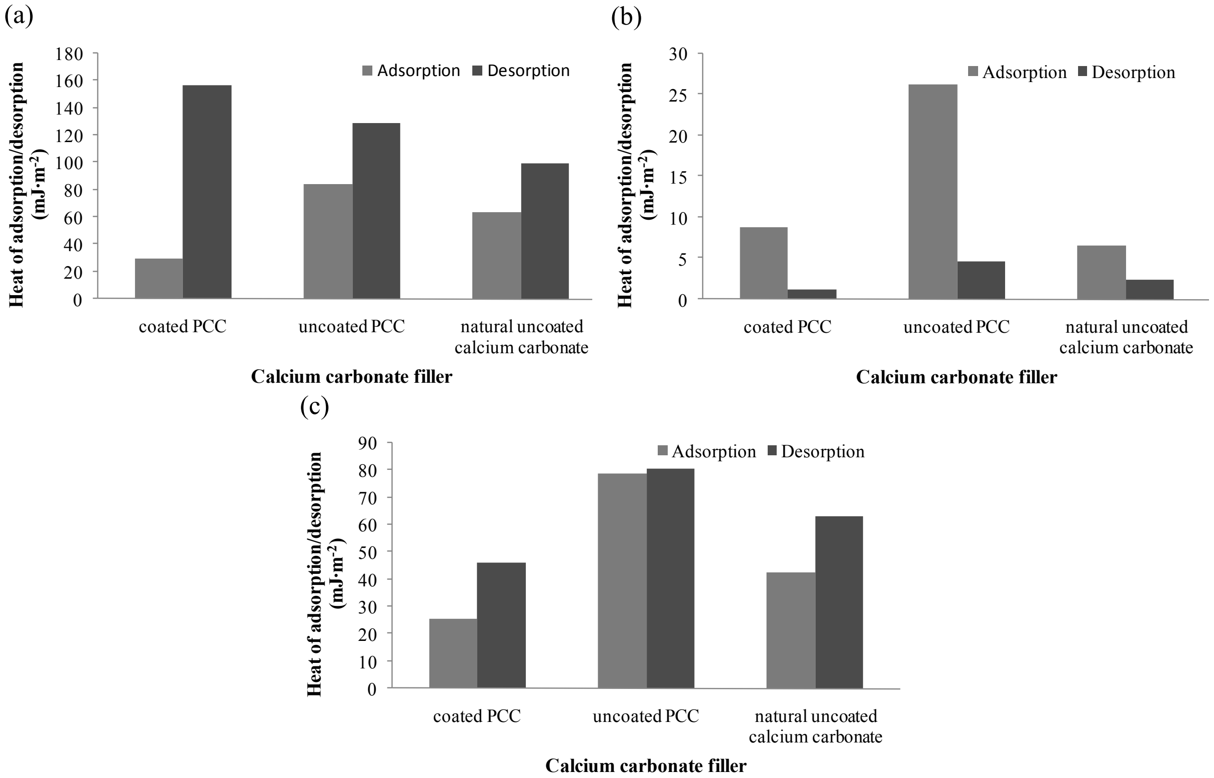

Figure 4. Heats of adsorption/desorption of indicated probes from indicated solvents on to the calcium carbonate samples: (a) dimethyl adipate from heptane; (b) dimethyl adipate from butan-2-one; (c) butan-2-one from heptane.

Figure 5 shows substrate subtracted spectra of dried fillers after adsorption and desorption of DA from heptane (Figure 5(a)) and butan-2-one (Figure 5(b)). The lower levels of adsorption from butan-2-one are immediately apparent as the ester carbonyl of samples where DA was adsorbed from butan-2-one is rather weak relative to equivalent samples where DA was adsorbed from heptane. In both cases, the two uncoated samples (PCC and GCC) show weak ester carbonyls that have been significantly shifted to lower energy indicating strong interaction of dimethyl adipate with the surface via its ester carbonyl groups. The coated PCC, however, shows a relatively large unperturbed carbonyl band at 1740 cm^{-1}. The absence of shifting of this band may be significant in that a large fraction of the carbonyls are not interacting with the coated PCC surface; but instead resting on, and within, the stearate coating. The fact that the carbonyl groups are not perturbed by the surface interactions may mean that they can vibrate more freely and therefore absorb more IR energy.

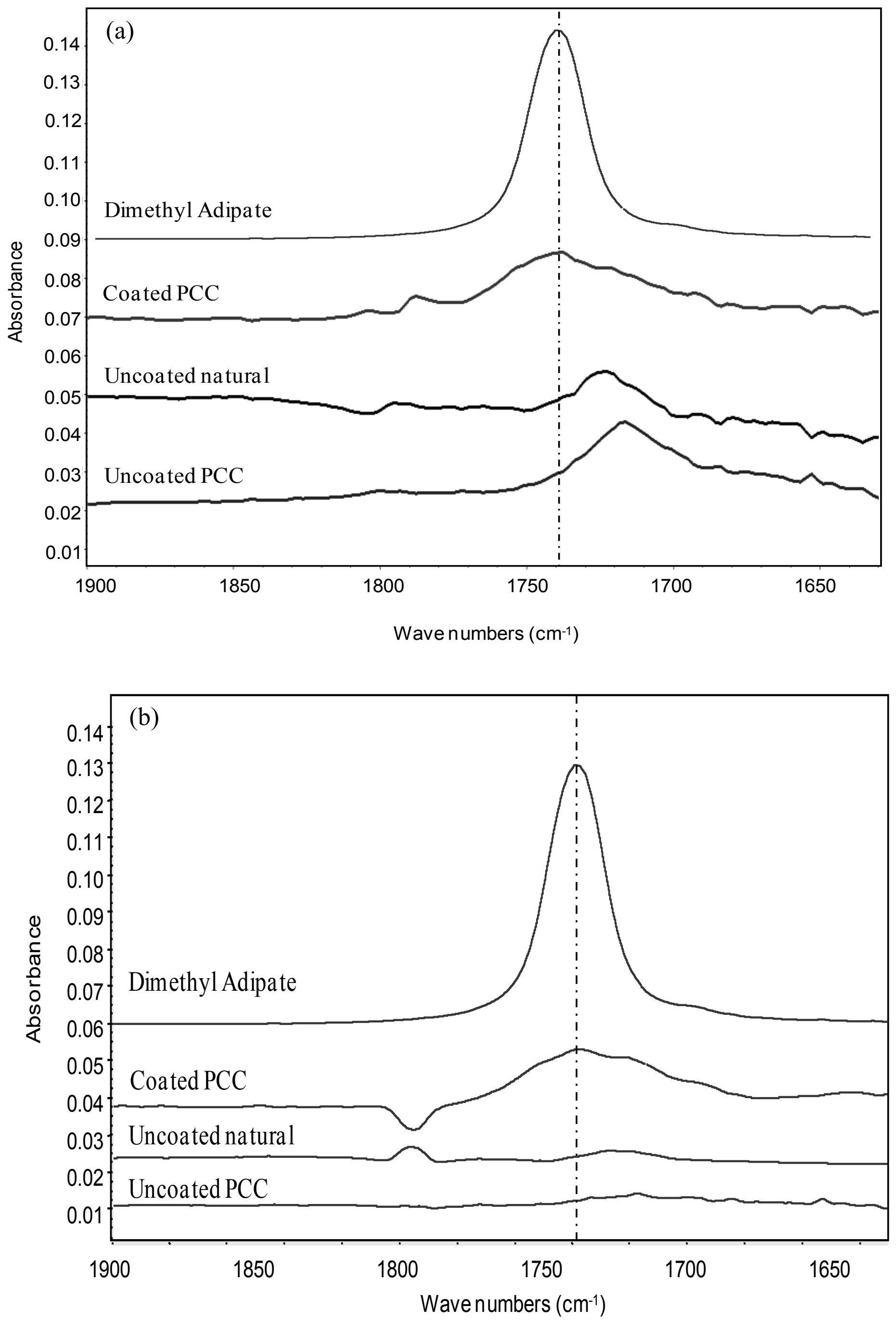

Figure 5. Substrate subtracted DRIFTS spectra of indicated samples isolated from the FMC cell after adsorption / desorption experiments; adsorptions from (a) heptane and (b) butan-2-one. The dimethyl adipate spectrum has been reduced to fit.

DRIFTS studies on solution adsorbed TPU

Due to the previously mentioned experimental problems associated with FMC adsorption of TPU, solution adsorption studies were carried out instead. Figure 6 shows a plot of A_{1731}/A_{1794} obtained from DRIFTS spectra of samples isolated from the adsorption flasks versus the level of TPU on the filler, which was calculated from the amount initially added. The ratio A_{1731}/A_{1794}, a measure of the amount of TPU adsorbed, increases more rapidly in the case of the uncoated PCC, thereby indicating stronger and more prolific interaction relative to that observed with the stearate treated PCC. This observation is entirely consistent with the FMC data for adsorption of DA, and the DMTA data for the TPU based composites. The difference in nature of interaction was also apparent from inspection of the carbonyl bands in substrate subtracted DRIFTS spectra (Figure 7). Before this discussion, it is important to note that the solvent subtracted spectrum of the TPU in solution shows a weak shoulder, assignable to the urethane carbonyls, at 1716 cm^{-1} on its main carbonyl ester band at 1729 cm^{-1}. Substrate subtracted DRIFTS spectra of the TPU on the unmodified PCC shows significant perturbation of the carbonyl bands to lower energy, when the addition level was below 0.00045 g/m^2. Though even at the highest addition level there is still significant band broadening with distinct skewing to lower energy. In contrast the equivalent spectra of TPU on the stearate treated PCC show rather more Gaussian-like peaks, at low TPU levels the degree of perturbation to lower energy is substantially less than with the equivalent unmodified PCC samples. Due to the close proximity of the ester and urethane carbonyl bands, together with the relatively low absorbance of the latter, it is not possible to distinguish whether or not the urethane groups are involved in adsorption. However, it is clear that interaction of the TPU with the untreated PCC in not hindered, and judging by the level of carbonyl perturbation, it is highly likely that the TPU is adsorbed relatively flat with a significant fraction of the carbonyl groups interacting with the GCC surface. The latter is particularly true when addition levels are low. It may be that adsorption of TPU on the stearate treated PCC may be more loopy in nature; only a small fraction of the carbonyl groups interacted with the PCC. This was due to blockage of a significant fraction of the surface by the adsorbed stearate. At high addition levels the TPU may be adsorbed on top of and amongst the adsorbed stearate anions.

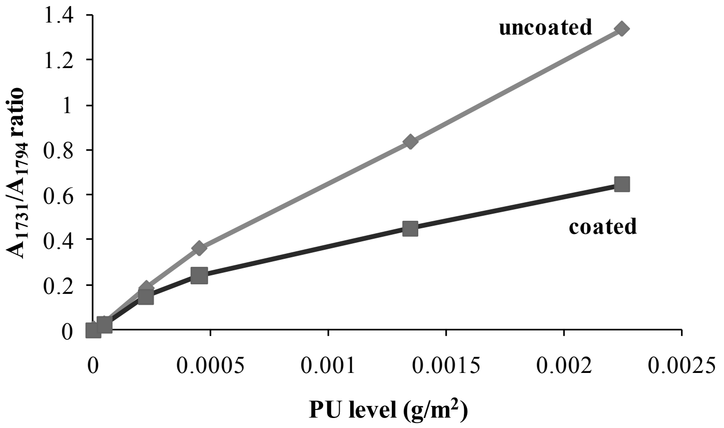

Figure 6. Variation of A_{1731}/A_{1794} ratio as a function of the PU level. A_{1731} means absorbance band area of ν_{st} C=O which corresponds to urethane and A_{1794} means absorbance band area of ν_{st} C=O which corresponds to calcium carbonate.

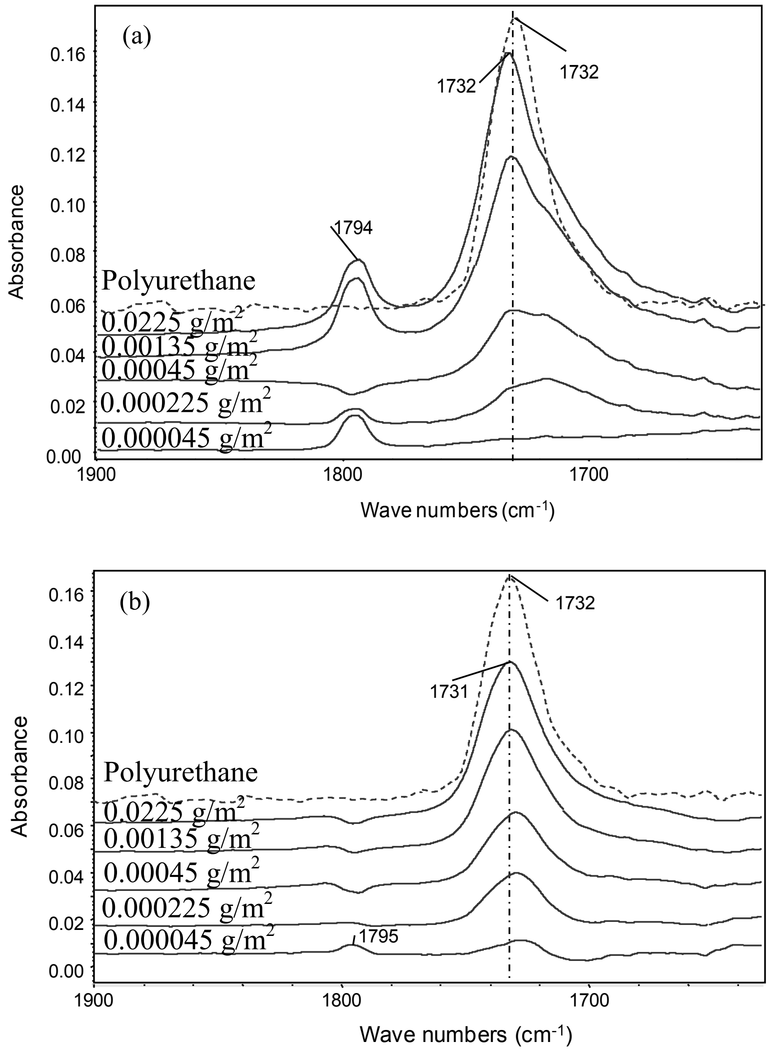

Figure 7. Substrate subtracted spectra of (a) uncoated PCC and (b) stearate treated PCC after adsorption of the indicated initial levels of TPU from butan-2-one. The TPU spectra have been reduced to fit.

Conclusions

TPU - calcium carbonate interactions can be predicted by conducting FMC adsorption studies on calcium carbonate using dimethyl adipate as a model for the polyester polyol segments of the TPU. The FMC studies were supported by DRIFTS analysis of samples isolated from the FMC cell and DRIFTS studies on uncoated and stearate coated calcium carbonates treated with varying levels of TPU. Both dimethyl adipate and the TPU strongly adsorbed onto untreated calcium carbonate via the ester groups. Stearate treatment of calcium carbonate greatly reduced the strength of interaction with the TPU due to blockage of the surface adsorption sites. DMTA studies were also conducted on TPU / calcium carbonate composites both the G′ and tan delta versus temperature data indicated that stearate modification of PCC led to significant reduction in filler-matrix interaction. The latter observation was entirely consistent with the adsorption studies.

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