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Flow micro-calorimetry and diffuse reflectance Fourier transform infrared spectroscopy studies in filled polyurethane adhesives by using dimethyl adipate as a model compound

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ABSTRACT

Interactions between nano-scale filler particles (precipitated calcium carbonate, carbon black and fumed silica) and model compounds (dimethyl adipate and butan-2-one) are quantified using flow micro-calorimetry (FMC) and diffuse reflectance Fourier transform infrared spectroscopy (DRFTIRS). Carbonyl groups of dimethyl adipate interact strongly with silanol groups on the fumed silica surface but weakly with the uncoated precipitated calcium carbonate. In general, higher surface area loading imparts high level of adsorption because of the nanofiller has more adsorption sites. Carbon black is an exception likely due to the less accessible surface groups and the presence of relatively important amount of micropores.

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1. Introduction

Over the past few years, nanofillers are incorporated to thermoplastic polyurethane (TPU) adhesives in the automotive, footwear and construction industry to improve their rheological, thermal, mechanical and adhesion properties. The performance of TPU-nanofiller material is related tightly to their interfacial interactions but detailed studies of such interactions are somewhat rare.

Thermoplastic polyurethane adhesives (TPU) are synthesized by reacting an isocyanate, a polyester, and a chain extender. TPUs show segmented structure composed of soft (non-polar hydrocarbon chain due to the polyester) and hard (polar, produced by reacting the isocyanate and the chain extender) segments, causing phase separation but their properties are dominated by the interactions between the soft segments, i.e. polyester chains. Addition of nanofillers may cause disruption of the phase separation [1,2]. Precipitated calcium carbonate (PCC), carbon black and fumed silica nanofillers have been used elsewhere for improving the rheological, mechanical and adhesion properties of thermoplastic polyurethanes [3–5]. The improved properties of some of these filled polyurethanes were ascribed to the existence of interactions by hydrogen bonding between the nanofiller surface and the polyol moieties. Thus, Vega-Baudrit et al. determined that the silanol groups on fumed silica and urethane groups in the polyurethane chains interacted by hydrogen bonding [6].

As a consequence of this, the soft segments were able to move freely and the phase separation increased. On the other hand, Luo et al. added nano-silicas modified with 3-methacryloxypropyltrimethoxysilane to polyurethane [7] and they found an increase in mechanical properties of the filled polyurethanes because of creation of covalent bonds between –C=O groups on modified silica surface and polymer chains. As a result, the movement of PU chains was limited and the creep resistance of polyurethanes was improved.

Parallel plate rheometry, dynamic mechanical thermal analysis (DMTA) and transmission electron microscopy (TEM) have been used to assess indirectly the nanofiller-polyurethane interactions but they are limited due to the absence of quantitative data at a molecular level. Peng et al. investigated the effect of adding modified carbon black on polyurethane foams [8]. They showed an increase in nanofiller–polymer chains interactions by using DMTA experiments.

In previous studies, precipitated calcium carbonate (PCC)-polyurethane interactions were assessed indirectly by parallel plate rheometry and DMTA experiments as well [5]. The addition of PCC increased the elastic modulus of the polyurethane slightly because of the existence of weak PCC–polyurethane interactions. In addition to this, the storage modulus was higher for filled polyurethanes and the glass transition temperature increased from $-23\,^{\circ}\mathrm{C}$ in the unfilled polyurethane to $-19\,^{\circ}\mathrm{C}$ in 20 wt% filled polyurethane. It is probably for the creation of Van der Waals interactions between the polyurethane chains and the surface of PCC particles, which reduce the movement of polyurethane chains.

In this study, the interfacial interactions between the polyurethane chains and the different nanofillers surfaces were studied with a more direct method, flow micro-calorimetry (FMC)

measurements supported by diffuse reflectance Fourier transform infrared spectroscopy (DRFTIRS).

FMC enables the measurement of the heats of adsorption and desorption of molecules in solution (and also in the gas phase) on to particulate solid surfaces. Attachment of the cell effluent line to concentration detectors allows determination of the levels of adsorption and desorption. As a result, FMC can be used to investigate and quantify interfacial interactions in composite materials [9–13]. In the existing literature, different fillers including carbon black, silica and organo-clays have been examined using FMC [11,14–16]. For instance, silica is able to interact with polar adsorbates via hydrogen bonding interactions with surface silanol groups (i.e., isolated, geminal, vicinal varieties) and siloxane bridges [17]. Nevertheless, some grades of carbon black and calcined silicas typically show Van der Waals or hydrophobic interactions with polymers [17]. Occasionally, polymer molecules can also be adsorbed and bond strongly at high energy sites on the carbon black surface [18].

In previously studies, Akoum et al. [19,20] investigated the effect of silica particle size and morphology, and surface energy on poly(dimethylsiloxane) elastomers adsorption. They established that the conformation of polymer chains on the filler surface and how they are connected had an influence on the adsorption phenomena. Additionally, the conformation of the macromolecules on silica depended on the silica surface area which was correlated with surface-polymer interactions.

Within the last five years FMC has been applied to studies of bio-diesel fuel manufacture, waste control, organic pollutants and catalysts, within the pharmaceutical, biochemical, chemical and polymer industries [21–25]. However, the use of FMC in studies of interfacial interactions in nanofilled thermoplastic polyurethane adhesive has not yet been reported in the literature. The aim of this study is to use a model compound to simulate the structural units of polyurethane. As the segmented structure of the thermoplastic polyurethanes is mainly dominated by polyester soft segments, in this study dimethyl adipate (DMA) was selected as a probe molecule to simulate the interactions between polyurethane chains and nanofillers of different chemical nature and surface chemistry.

2. Experimental

2.1. Materials

Two coated (Socal®312) and uncoated (Socal®312) precipitated calcium carbonate (PCC, supplied by Solvay Specialités, Salin de Giraud, France), carbon black (CB) (Corax®N134 supplied by Evonik, Essen, Germany), and fumed silica (Aerosil®200 supplied by Degussa, Hanau, Germany) were used as nanofillers. Some properties of the nanofillers are given in Table 1 [26–28]. All fillers have a mean particle size in the nanometer range, and it is related to their specific surface area. Thus, the fumed silica has the smallest mean particle size and the highest specific surface area, and the PCCs have the biggest mean particle size and the lowest specific surface area.

2.2. Experimental techniques

2.2.1. Transmission electron microscopy (TEM)

A Jeol TEM-2010 instrument (Tokyo, Japan) was used to analyze the topography, shape, particle size and degree of agglomeration of the nanofillers; an acceleration voltage of 100 kV was used. The samples were prepared from low concentration suspension of filler particles in ethanol up to obtain a translucent dispersion, and then it was mixed in ultrasonic bath for 4 min. A drop of the

Table 1
Some properties of the nanofillers.

Nanofiller	Specific surface area [$m^2 g^{-1}$]	Mean particle size[a] [nm]
Coated precipitated calcium carbonate	19	70
Uncoated precipitated calcium carbonate	20	70
Carbon black	159	< 20
Fumed silica	225	12

[a] Data taken from the technical data sheets [26–28].

suspension was put on Lacey grid of 3.05 mm of diameter, followed by ethanol evaporation at room temperature.

2.2.2. N_2/77 K adsorption–desorption isotherms

The adsorption–desorption isotherms of the nanofillers were obtained in the Quantachrome Instrument adsorption system (Quantachrome, Florida, USA). Prior adsorption measurements, the filler was outgassed at 150 °C for 12 h at a residual pressure of 10^{-6} Torr. From adsorption data, specific surface area of nanofillers was obtained by using the B.E.T method and the Eqs. (1) and (2), where V_m is the adsorbing volume in a monolayer, C is the parameter due to gas–solid interactions, P is the equilibrate pressure, P_0 is the saturated pressure, V_{ads} is the N_2 adsorbing volume, a_m is the area of one molecule of N_2 (16.2×10^{-20} m^2), N_A is Avogadro's number, and V_M is molar volumen of adsorbate (22414 cm^3 mol^{-1}).

$$\frac{P}{V_{ads(P_0 - P)}} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C}\frac{P}{P_0} \tag{1}$$

$$S_{BET} = \frac{a_m V_m N_A}{V_M} \tag{2}$$

2.2.3. Thermal gravimetric analysis (TGA)

The mass loss of the nanofillers as a function of the temperature was measured in TGA Q500 instrument from TA Instruments (New Castle, Delaware, USA). The samples (10–15 mg) were placed in platinum pans and were heated from room temperature to 800 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere (flow rate: 100 ml min^{-1}).

2.2.4. Flow micro-calorimetry (FMC)

The FMC instrument used was a Microscal 3 V with polytetrafluoroethylene (PTFE) cell (MICROSCAL Ltd, London, UK). The cell outlet was connected to a Waters 410 differential refractometer (MILLIPORE, Massachusetts, USA). 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), and the experiments were carried out at cell temperature of 20 ± 1 °C. Adsorption experiments were carried out from both heptane and butan-2-one because heptane is the most common solvent used in FMC and butan-2-one is the typical solvent for polyurethane adhesives formulation, at a flow rate of 4.0 ml h^{-1}. The concentration of the probe solution was 0.3 vol%. Decahydronaphthalene was used as the non-adsorbing probe.

The butan-2-one and heptane were HPLC grade (Lab-Scan Analytical Sciences, POCH S.A., Gliwice, Poland) and were dried over 3A molecular sieves. The adsorption and desorption of dimethyl adipate (99%, Aldrich, Dorset, UK) on to the nanofillers in heptane or butan-2-one was carried out at 20 °C according to established FMC methods [10,13–17,19,20,24,25]. After completion of the FMC experiments, the nanofillers were oven dried at 70 °C